ELEMENTARY PRINCIPLES OF CHEMISTRY

BROWNLEE TULLER HANCOCK SOHON WHITSIT

REVISED EDITION

Beale

11 John

~~Arley Edgerton~~

Johnny
~~Edgerton~~

Elizabeth Godwin

Sr. V-VI

1935-1936

21-5

Open Face Oil Engine

135

Valence- Combining Power

Elizabeth Godwin.

Sr. 6-6 — 1936-36

1 —

Milli - 1/1000
Centi - 1/100
deci - 1/10
deca - 10
hecto - 100
kilo - 1000

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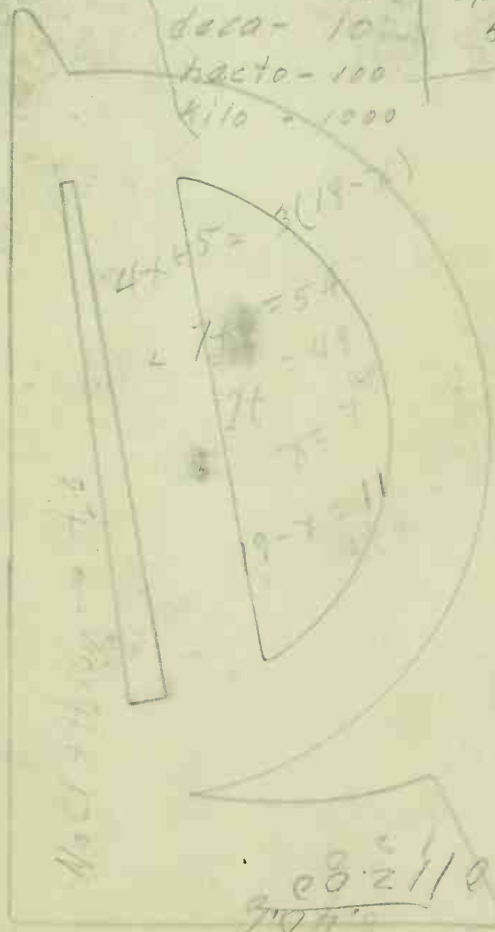

$H_2SO_4 + C_6H_{12}O_6 \rightarrow H_2O + C_6$

Smelting of iron ore

1. $C + O_2 \rightarrow CO_2$
2. $CaCO_3 \rightarrow CO_2 CaO$
3. $CaO + SiO_2 \rightarrow CaSiO_3$ (Slag.)
4. $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

Amphoteric elements

Al	Sb	Be
Zn	Pb	Zn
Sn	Ps	

Unsaturated hydrocarbon - replacement + addition

Saturated " -

Elizabeth Godwin.

March 18, 1936

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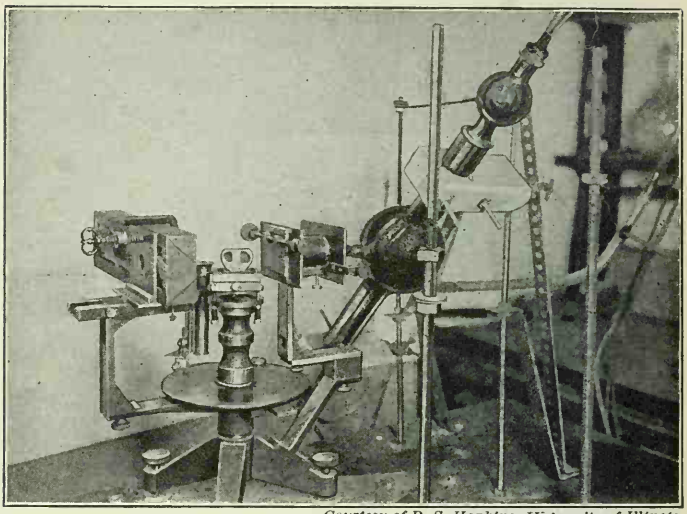

Courtesy of B. S. Hopkins, University of Illinois.

SEARCHING WITHIN THE ATOM.

Apparatus like this is used to find out the inside structure of an atom. X-rays are generated in the bulb tube on the right. These fall on the crystal which rests on the little stand in the middle; from the crystal, the X-rays are reflected in a pattern which depends on the constitution of the particular atom which is being studied. The pattern is photographed on a plate in the box at the left.

This is the apparatus used by B. S. Hopkins of the University of Illinois in making certain that he had found a new element, whose atomic number is 61, to occupy a hitherto vacant place in the table on page 120. The new element bears the name *illinium*, in honor of the state which supports the University where the work of discovery was carried out.

ELEMENTARY PRINCIPLES

OF

CHEMISTRY

REVISED

BY

RAYMOND B. BROWNLEE
STUYVESANT HIGH SCHOOL

ROBERT W. FULLER
STUYVESANT HIGH SCHOOL

WILLIAM J. HANCOCK
ERASMUS HALL HIGH SCHOOL

MICHAEL D. SOHON
MORRIS HIGH SCHOOL

JESSE E. WHITSIT
DE WITT CLINTON HIGH SCHOOL

ALL OF NEW YORK CITY

Elizabeth Godwin. N.Y.
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ROBERT W. FULLER, WILLIAM J. HANCOCK
MICHAEL D. SOHON, AND JESSE E. WHITSIT

FID

PRINTED IN THE UNITED STATES OF AMERICA

If my name you do not see
look on page 403

PREFACE

This new revised edition has been undertaken largely because the electron theory of the atom has established itself firmly in the science of chemistry. This theory explains why elements combine with each other and answers the question which Lord Kelvin, after fifty years devoted to science, regretted he could not solve. It gives a sound basis for valence and helpful images for use in picturing how valence works. Atomic numbers give even young pupils a key to the classification and properties of the elements.

This new hypothesis makes chemistry easier to teach, not more difficult. Chemists no longer think of solids as made up of individual, separated molecules, and the Revised Chemistry adopts this up-to-date conception. These matters are presented in language simple enough for easy comprehension and actual classroom tests have proved that these points can be successfully taught.

The attention of teachers has long been directed to the large number of technical terms in chemistry, and many have contended that much of the difficulty of the subject is due to these. This revised edition omits many such terms, and in all cases a technical word is used only after the essential idea has been thoroughly presented in familiar language.

The authors realize that a constant danger in chemistry is the mechanical teaching of memorized facts and processes. They feel that the development of mental habits ought to receive increased attention. So, while the book contains

plenty of fact questions to aid the teacher in drill and in assigning home work, the authors have restudied their power questions, aiming to make them simple enough to be within the pupils' grasp, and numerous enough to promote the objective of individual thinking.

It will be noted that the new edition uses 22.4 liters as the gram-molecular volume. This change, which bases chemical calculation definitely on the atomic weight of oxygen taken as 16 instead of on hydrogen as 1, is a consequence of the electron theory. It is now known why atomic weights are generally whole numbers, so placing oxygen at 16 is not only convenient, but logical as well.

In this new edition *Elementary Principles of Chemistry* continues to stress the social service of chemistry. In addition, the authors have had in mind the spiritual value of chemistry and have pointed out the necessity of using imagination in science. It is believed that chemistry has pre-eminent value as a means of teaching intellectual integrity, especially through the unusual ease with which its laboratory work can reproduce facts. The laws of chemistry are definite, thoroughly proved, and easy of exemplification. No subject tends more to show the world as a place of law and order.

FROM THE PREFACE TO THE FIRST EDITION

CHEMISTRY is decidedly a living, growing subject; research brings new facts to light, new, helpful theories into being; experience points the way to clearer, simpler statement. In writing this book, however, we have recognized the fact that a very general agreement of opinion as to the content of elementary chemistry still continues. Suggestions generously sent by fellow workers from all parts of the country have indicated possible improvements; and these have been freely embodied in this book.

We have not departed in any essential way from our guiding principles for making this sort of book. A restatement of them may not be out of place here:

1. A proper study of science must lead to generalizations.

2. In reaching these generalizations, the historical order of development probably indicates the easiest path of approach for the immature mind.

3. Theoretical matters should not be presented in too large doses at one time.

4. Industrial processes sometimes serve better for the teaching of chemical principles than do laboratory experiments.

5. Detailed descriptions of experiments, long explanations, particularly the kind usually put in fine print, cumber the text and act as barriers to acquiring essential facts.

ACKNOWLEDGMENTS

THE authors are indebted to many firms and individuals, as indicated in the body of the text, for material used in making illustrations. In addition, they wish to extend thanks to Mr. Allen B. Doggett for aid in photographic work, to Mr. George Wright for adaptation of the drawings used in showing steel furnaces; to the Samuel M.. Green Co. for the illustration of the Edgewood chlorine-caustic soda plant designed by them; to Mr. Jerome Alexander for suggestions concerning our treatment of colloids; and to Mr. Herbert B. Tschudy for an oil painting showing a copper furnace in operation. Others who have given generous assistance are: Professor Charles F. Chandler of Columbia University, Professor Harmon N. Morse of The Johns Hopkins University, Professor L. H. Merrill of the University of Maine, Mr. Ben M. Jaquish, Mr. C. D. MacArthur, Mr. Duncan McArthur, the Nitrate Division of the War Department, the American Smelting and Refining Co., Eimer and Amend, the Oxweld Acetylene Co., the Warner Chemical Co., the L. M. Booth Co., the Brooklyn Gas Co., the Carborundum Co., the National Lead Co., the Standard Oil Co., the Union Sulphur Co., Jacobson Bros., and Mr. Robert A. Bright.

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ELEMENTARY PRINCIPLES OF CHEMISTRY

INTRODUCTION

THE first part of the twentieth century saw enormous developments in the chemical industry throughout the world. During the Great War, the needs of the time compelled a self-reliance that placed our chemical industries on a firm foundation, both as to variety of products and capacity for production. In addition to the poison gases, explosives, and many other chemical products used directly in warfare, this country was obliged to produce enormous quantities of glass, dyes, photographic chemicals, and pharmaceutical preparations, which were formerly imported from Europe.

As a permanent result of this situation, we realize that we are not compelled to rely upon foreign nitrates and potash deposits. Processes have been developed for making from the air nitrogen compounds suitable for plant food. The working of certain saline deposits and, more particularly, the recovery of the potassium compounds from the flue dust of cement kilns and blast furnaces may yield thousands of tons of potash.

Dyes of excellent quality are made in such quantity that we export to other countries after supplying our own needs. The United States now bids fair to become a strong competitor for that trade in the markets of the world.

American porcelain, high grade chemical glassware, optical glass, and silica products are manufactured in large quantities. Improved types of chemical machinery and the con-

struction of vast plants have brought chemical manufactures to a foremost place in the country's industries. The establishment of chemistry on a sound basis as one of the great permanent industries of the country, equipped for production on a large scale, has increased the demand for skilled chemists and trained chemical engineers, as well as for a host of intelligent workers in the plants. The dependence of the country on the services of the chemist, however, is not yet

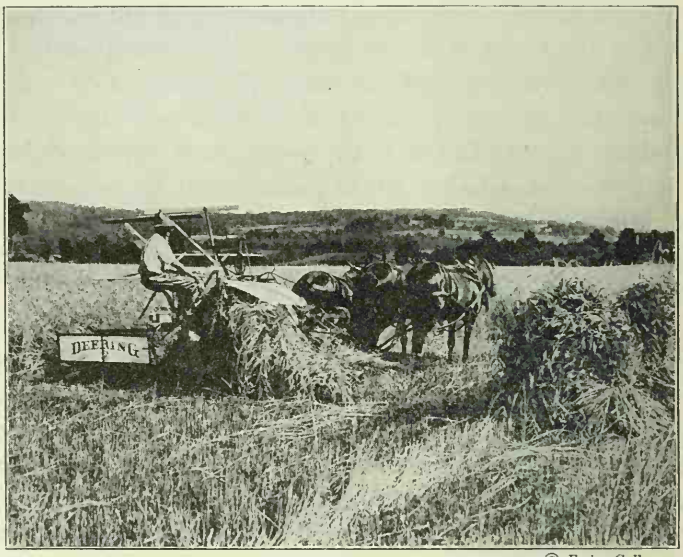

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FIGURE 1.

In nature's vast chemical laboratory carbon dioxide and oxygen are taken from air, and, with the aid of water and minerals from the soil, are transformed into grains of wheat.

fully appreciated; nor is there sufficient general realization of the additional contributions chemistry may still make, not only to our physical comfort, but also to our intellectual and our spiritual welfare.

CHAPTER I

CHEMICAL CHANGE

1. Chemical Change. — Most of the things to which we are accustomed are not found naturally in the condition in which we know and use them. Our foods, for example, are

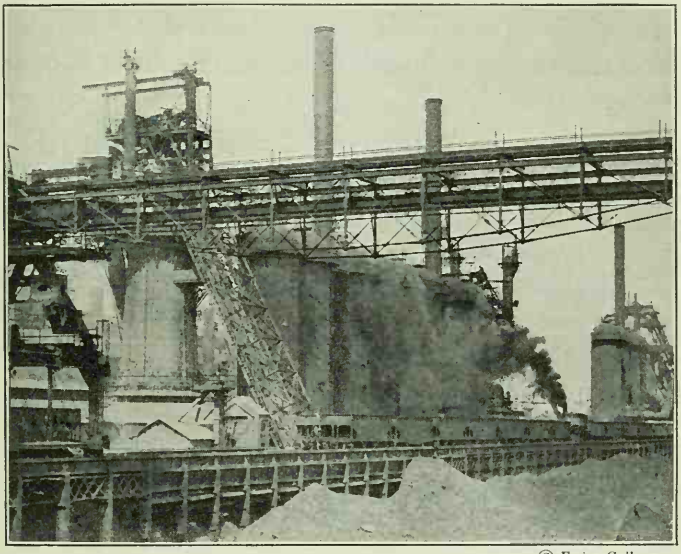

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FIGURE 2.

Here is one of man's largest laboratories. A reddish earth is heated with coke made from coal, and limestone, or other earthy matter. Iron is thus produced abundantly.

derived from plants, which take their substance from the earth and the air (Fig. 1). Iron is obtained from a reddish earth (Fig. 2) and aluminum from a white substance, neither

of which suggests a metal. As we have advanced in civilization, we have adapted many materials to our needs and comfort.

Iron rusts, silver tarnishes, milk sours, fruit decays. New substances are formed in these actions and such changes are called *chemical changes.*

A chemical change is a change in which a substance loses the characteristics by which we identify it. New material with new characteristics is formed.

Chemistry is the name given to the science that has grown out of the study of chemical changes and the effort to control or modify them.

2. Nature of Burning. — The most striking of the chemical changes that go on about us is that which occurs when a substance burns. If the burning substance is coal or wood, it seems to disappear except for a small quantity of ashes.

Early investigators did not discover the true nature of this process. They adopted a wrong explanation, and as a result, the science of chemistry did not advance. The modern interpretation was stated only about a century and a half ago. Since that time, chemistry has progressed at an astonishing rate. The true explanation of burning was found by studying the change that many metals undergo when heated in air.

3. Heating Metals in Air. — Some metals, for instance magnesium, burn when heated in the air. Most metals undergo a similar but much slower change, without the production of light. If a piece of bright copper is heated, it assumes a black color; when bent or scraped gently, a black powder separates from it. If the metal is heated again, another layer of the black substance forms. By

repeating the process many times, the piece of copper can be entirely changed into the black powder. This black powder in no way resembles the original piece of copper.

Melted lead slowly turns into a yellowish powder; zinc, if in the form of a powder, will take fire when heated and yield a white powder. While gold, silver, and platinum show no change on being heated in air, most other metals when thus treated produce powdered substances bearing little or no resemblance to the original metal. In all these changes, the metals have lost their identity, and substances with new characteristics have been formed. Such alterations are called *chemical changes*. We see many changes, however, in which new substances are not formed. Such changes are called *physical changes*. Turning wood into sawdust and heating a wire with an electric current are examples of physical change, because the sawdust is still wood, and the wire remains just as it was, after the current ceases to flow.

4. The Product Weighs more than the Metal. — Several things may be thought of as explanations of the change which the metals undergo. It may be that, by the effect of the heat, without the aid of any substance, the metal is transformed into a new kind of matter; possibly the metal in being heated has lost some of its substance, which has passed off as gas; possibly the metal has absorbed something from the air.

To help in testing these possible explanations, it will be advisable to weigh the metal before and after it is heated. When this is done, it will be found that *the powder always weighs more than the metal* from which it was formed. This seems to indicate that, during the heating, the metal adds

to itself more substance, and that this substance is taken from the air. To further test this conclusion, a piece of metal can be sealed in a glass tube from which the air has been exhausted; *heated under these conditions, the metal is not changed into anything else.*

5. Lavoisier's Experiment. — Lavoisier, the French chemist, to whom is given the credit of discovering the nature of this kind of chemical change, put some tin into a good-sized glass flask which he sealed so that air could neither enter nor leave it. He then heated the flask carefully for several days. At the end of this time, he noticed that a certain amount of white powder had been formed. He next ascertained that the flask with its contents had not changed in weight. He then opened the neck of the flask and noticed that air rushed in. On again weighing the flask and its contents, he found that there was an increase in weight. He explained these facts as follows: the tin on being heated combined with some of the air in the flask, producing the white powder. The flask as a whole did not increase in weight, because no air entered the flask to take the place of that which had combined with the tin. When the flask was opened, the air entered, causing the increase in weight. This was equal to the increase in weight of the tin when it was converted into the white powder.

Since experience has shown that matter is never created nor destroyed, it appears probable that the powdered substances are more complex than the metals from which they are formed; that is, they contain the metal plus something which has been taken from the air.

6. Heating Mercury in the Air. — Lavoisier undertook to find out the nature of the substance which was taken

Antoine Laurent Lavoisier (1743–1794) was a French investigator and scientific interpreter. When twenty-five, he was chosen adjunct member of the French Academy, and became one of the leading scientists of his time.

Lavoisier studied combustion and showed by quantitative experiments that the weight of the product exceeds the weight of the fuel. He explained the composition of air and of water and advanced the doctrine of indestructibility of matter.

Joseph Priestley (1733-1804) was an English writer on religion, politics, and science. He was a brilliant investigator and experimenter. His experiments suggested to him that plants and animals produce opposite changes in the air.

Priestley discovered several gases, notably oxygen. This he prepared by heating mercury oxide.

The latter years of Priestley's life were passed in Pennsylvania.

from the air. Mercury, heated in the air, undergoes a much less rapid change than the metals of which we have been speaking. For several days Lavoisier kept some mercury at a temperature a little below its boiling point and obtained a small quantity of red powder (Fig. 3). He then heated a quantity of this powder in a glass tube to a temperature above the boiling point of mercury, and a colorless gas was given off. This experiment had also previously been performed by Priestley.

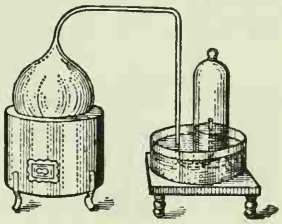

FIGURE 3.

The apparatus in which Lavoisier made mercuric oxide. Mercury was put into the large flask and heated on a charcoal stove. Water slowly rose in the bell jar, proving that a part of the air was consumed in the reaction.

A glowing splinter was inserted into the gas. The splinter burst into flame and burned brilliantly. The gas could not have been ordinary air, for a glowing splinter does not begin to burn with a flame so long as only air is present. A quantity of the gas was collected and was shown to be very different from ordinary air by the fact that substances burned in it with extraordinary vigor.

On examining the tube, it was found that a part or all of the red powder had disappeared and that drops of mercury had collected on the sides of the tube. It appears from this experiment that *the red powder had decomposed into mercury and a gas* which readily supports combustion. Lavoisier named this gas *oxygen*.

7. Heated Mercury Takes Oxygen from the Air. — Since the red powder was made by heating mercury in the air, and was not formed unless air was present, *the*

oxygen must have come from the air. Hence air must contain oxygen. That air is not all oxygen is shown by the fact that only about one fifth of the air, not all of it, was absorbed in Lavoisier's experiments; and also by the fact that substances do not burn as readily in air as in oxygen.

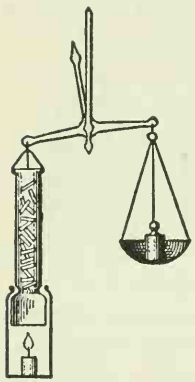

FIGURE 4.

If all the products of the burning of any substance are caught, they weigh more than the original material. Here it is a candle which burns; all the products are absorbed by the pieces of sodium hydroxide which fill the upper part of the lamp chimney.

The powders obtained by burning tin or copper or iron weigh more than the original piece of metal because the metal combines with a noticeable weight of oxygen from the air. It is not possible to separate these metals from the oxygen by heating at the temperatures that are commonly used in the laboratory.

8. Burning. — When wood or other substances burn the process closely resembles the change of a metal into a compound of the metal and oxygen. In the case of ordinary combustible materials, the products are chiefly gases which pass off unseen. By the use of suitable apparatus (Fig. 4), the products formed in the burning of a candle can be collected, and it is found that their weight is greater than the weight of the candle burned. As in the case of the metals, this increase in weight is due to the oxygen taken from the air.

The failure to observe and collect the gaseous products of ordinary burning was partly responsible for the inability of the early investigators to give a correct explanation of the true nature of burning.

9. Solids, Liquids, and Gases. — Metals, powders, air, and oxygen are forms of *matter*. Matter is generally defined as anything that occupies space. The different kinds of matter are called *substances*. Substances differ in the way they fill space, and it is this difference that determines their *physical state*. The three physical states of matter are the solid, the liquid, and the gaseous.

A *solid* has a definite shape or *form*, and a definite *volume*. A *liquid* has no definite form, but has a definite volume. It can fill a vessel only to the extent of its volume and takes the shape of the containing vessel so far as the liquid fills it. *Gases* have neither a definite form nor a definite volume. They distribute themselves in all directions and fill completely any vessel into which they are put. Their only boundaries are the containing walls. Most substances, under suitable conditions of temperature and pressure, can be obtained in all three states — as solid, liquid, or gas.

10. Identifying Substances. — All substances have many characteristics or properties. Different kinds of matter are recognized by their peculiarities.

Some of the physical properties used in identifying substances are:

Solid State	Liquid State	Gaseous State
Density (relative weight);	Density (relative weight);	Density (relative weight);
melting point;	freezing point;	
luster;	boiling point;	condensing point;
hardness;	viscosity;	
color, taste, or odor;	color, taste, or odor;	color, taste, or odor;
solubility.	solubility.	solubility.

Chemical properties used in identifying substances are:

Reactions with air or oxygen;

Reactions with water;

Reactions with acids or bases;

Other reactions peculiar to the substance or its constituents.

11. Elements. — Before the discovery of radium there were about eighty substances that had not been decomposed. These substances were regarded as simple substances, or *elements*. *An element is a substance that has not been separated into other substances by chemical action.* With knowledge gained from the study of radium and by the use of high voltage electric discharges, scientists have been able to get evidence of the change of one element into another. A list of important elements is given in Table I, Appendix.

Chemists divide elements into two classes, the *metals* and the *non-metals*. Examples: iron, copper, and silver are metallic elements; oxygen and sulphur are non-metals.

12. Compounds. — We have shown that the red powder formed by heating mercury in air contains oxygen and mercury. The substance formed on heating copper in the air contains oxygen and copper. As these substances are composed of more than one element, they are called *compounds*. *A compound is a substance that can be separated by chemical action into two or more simpler substances.*

13. The Names of Elements are not based on any principle. Some, like sulphur and silver, are very old; some are named for countries or localities, for example, magnesium and columbium. Soda and alum were well-known compounds, and when metals were obtained from them these received the names of sodium and aluminum. Other ele-

ments have been named in similar manner. Chlorine, argon, radium, and chromium are named from peculiarities possessed by them, while selenium (moon), tellurium (earth), and uranium (heaven) show that chemists have not been without poetic fancy.

Of the elements discovered more recently, the metals have received names ending in **-ium**, the non-metals in **-n** or **-ne**. Names have usually been assigned the elements by their discoverers and are carried practically unchanged into other languages.

SUMMARY

A **chemical change** is a change in which a material loses the characteristics by which we identify it. Chemical changes involve changes in the identity of the material.

A **physical change** is a change in which a material does not lose the characteristics by which we recognize it.

When a substance burns in air, it undergoes chemical change by combining with oxygen.

Lavoisier obtained oxygen from air by heating mercury in it and then decomposing the material produced.

An **element** is a substance which has not been separated into other substances by chemical action. There are two kinds of elements: metals and non-metals.

A **compound** is a kind of matter that can be separated into two or more substances.

Names of metallic elements usually end in **-ium**, those of non-metals in **-n** or **-ne**.

EXERCISES

1. Air and water were formerly called elements. Why are they not now?

2. How could you prove that air contains oxygen?

3. Distinguish between a chemical change and a physical change.

4. What kind of change is involved in making cloth from wool? Baking bread? Burning coal? Extinguishing the fire? Rusting of iron? Decay of fruit? Fermenting fruit juices?

5. Describe experiments that you performed in the laboratory which illustrate the difference between physical and chemical change.

6. Distinguish between the terms *element* and *compound.*

7. When 2 grams of a certain substance were heated, all the oxygen which the substance contained was given off, and a residue weighing 1.07 grams was left. Calculate the percentage of oxygen in the substance.

8. Why is the crushing of glass not a chemical change?

9. Name three chemical changes that occur in the kitchen; three physical changes.

10. What kind of changes are involved in: The digestion of food? The raising of your arm? The ripening of fruits? The paring of potatoes?

11. What is the particular difficulty in proving that the products formed by burning a candle weigh more than the candle?

12. What always happens when a substance burns in air?

13. How did the failure of the earlier investigators to use a balance prevent them from finding the true explanation of burning?

CHAPTER II

OXYGEN

14. An Abundant Active Element. — Civilized man knows that no element is more important to his existence and well-being than oxygen. It is nearly a quarter of the weight of the great ocean of air at the bottom of which we live, and eight ninths of the weight of all the waters of the earth. Oxygen unites with so many elements that we cannot dig anywhere into the crust of the earth without encountering its compounds. Fully half of the surface material of the earth is oxygen in combination with other elements.

Animals and plants need a constant supply of this element to continue their life activities. The cooking of our food, the warming of our homes, and the development of mechanical power are dependent upon oxygen. This very active element fascinates us with its wide range of chemical reactions, varying from its quiet combination with iron in rusting to its terrifying activity in explosions and conflagrations. In the laboratory, we study at close range many of the actions of oxygen.

15. Discovery. — In 1774, Priestley obtained oxygen from a red powder prepared by heating mercury in air. When this powder is heated at a temperature somewhat higher than that at which it was made, it is decomposed into a gas, oxygen, and a metal, mercury. This is an easy way to get small quantities of the gas, but is too expensive a method for practical use in obtaining larger amounts.

16. Preparation. — The common laboratory method for preparing oxygen is by heating potassium chlorate, another substance that needs but little heat to make it give off its oxygen (Figs. 5, 6). This compound, composed of potassium, chlorine, and oxygen, melts when heated and then gives off oxygen gas, leaving a residue of potassium chloride, which is a compound of potassium and chlorine. We may express this change by a word equation:

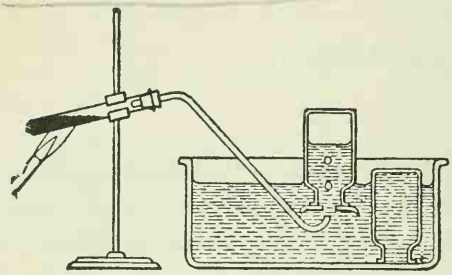

FIGURE 5.

The mixture in the test tube contains potassium chlorate and manganese dioxide. When it is heated, oxygen issues from the delivery tube and is collected in bottles previously filled with water and inverted. At the end, we find the potassium chlorate turned into potassium chloride; but the manganese dioxide remains unchanged.

potassium chlorate ⟶ potassium chloride + oxygen

The arrow is to be read *yields* and the + sign, *and*.

It is customary to mix the potassium chlorate with manganese dioxide, because the decomposition then takes place at a lower temperature and goes on more evenly. A material that thus changes the speed of a chemical action, *without being permanently altered itself*, is called a *catalyzer* or catalytic agent. In this one case, manganese dioxide is a catalyzer; *in all other cases* where we shall use manganese dioxide, it is permanently changed in the chemical reaction.

Oxygen is prepared on a commercial scale by passing an electric current through water (§ 30) or through a water

solution of sodium hydroxide. A cheaper method, however, is by liquefying air and letting its nitrogen, which boils off at a lower temperature than oxygen, escape first.

17. Collection of Gases. — Gases are generally collected in the laboratory by the displacement of air or of water. The second is the better method whenever it can be used, because air, being a gas, mixes easily with other gases. Oxygen is not very soluble in water and hence may be conveniently collected over this liquid.

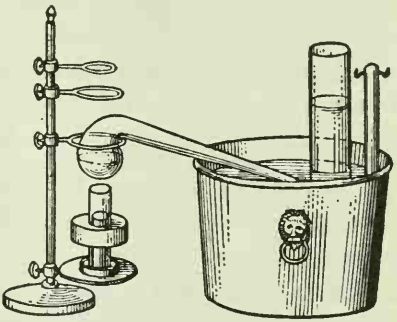

FIGURE 6.
Apparatus used a hundred years ago in preparing oxygen.

It seldom happens that the products of any chemical action are obtained free from impurities. In getting oxygen from potassium chlorate, a whitish dust is often carried from the generator along with the oxygen. On standing, this dust will settle into the water, leaving the oxygen as a colorless gas.

18. Physical Properties. — The physical properties of pure oxygen are not striking. It is a gas without color, odor, or taste, and is a little heavier than air, volume for volume. Oxygen is but slightly soluble in water; under ordinary conditions, 100 volumes of water dissolve only about 3 volumes of oxygen. But this small amount of dissolved oxygen in natural waters is of great importance. Fishes could not breathe without it; it makes our drinking water more palatable; it converts into inoffensive materials de-

caying animal and vegetable matter in our streams, rivers, and harbors. When much sewage is emptied into the waters around large cities, the amount of dissolved oxygen may be reduced below the safety limit.

The presence of dissolved oxygen in water may be shown by allowing ordinary faucet water to stand in a glass. As the water gets warmer, bubbles will be observed clinging to the sides of the glass. Such bubbles are largely oxygen that was dissolved in the water while it remained cool.

When compressed and cooled sufficiently, oxygen condenses to a pale-blue liquid; on still further cooling, it solidifies.

19. Chemical Properties. — The most noticeable chemical property of oxygen is its *tendency to combine with other elements.* At ordinary temperatures, it does not readily react with many substances, but at higher temperatures its action is rapid, and is usually accompanied by noticeable heat and light. Nearly all elements combine readily with oxygen to form oxides.

20. Oxides. — *An oxide is a compound of oxygen and another element.* The red powder of Lavoisier is mercury oxide, since it is a compound of the two elements mercury and oxygen. The oxides of metals are solids, but a number of oxides, such as the carbon dioxide of the air, are gases. Water is hydrogen oxide, a liquid. *A chemical action in which a substance unites with oxygen is called oxidation.*

21. Combustion *is any chemical action by which noticeable heat and light are evolved.* In *ordinary burning* a substance unites with the oxygen of the air. When the action takes place rapidly, the increase in temperature is appreciable, and light may result (Fig. 7). Thus, when a piece of coal burns, the carbon of the coal combines with the oxygen of the air to

form carbon dioxide, a gas which passes off unseen; at the same time a considerable quantity of heat is evolved, and the neighboring particles of fuel become red-hot.

FIGURE 7.
Phosphorus burns in oxygen with dazzling brilliancy.

As the air is only about one fifth oxygen, substances do not burn as readily in it as in pure oxygen. A glowing splinter plunged into oxygen bursts into flame. Charcoal glows much more brilliantly in oxygen than in air. Sulphur burns in air with a pale-blue flame; in oxygen vividly. Iron burns in oxygen with dazzling scintillations.

A gas in which a substance will burn is said to *support*

FIGURE 8. © *Ewing Galloway.*

A chemical action, perhaps started carelessly by some human, has got beyond control and is destroying beauty as well as property. Oxygen in the air supports the combustion.

combustion. Oxygen is the most common supporter of combustion. It is because air contains oxygen that ordinary fires are possible (Fig. 8).

Ordinary burning is oxidation accompanied by noticeable light and heat.

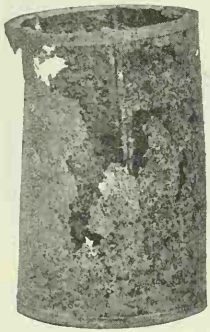

FIGURE 9.

This shows what happens to iron when it is left exposed to the weather. By slow oxidation iron is converted into iron oxide and other compounds of iron.

22. Slow Oxidation. — Oxidation is not always accompanied by light or even by noticeable heat. Thus, when iron rusts (Fig. 9), it slowly combines with oxygen. When wood decays, the materials produced are nearly the same as those formed when it burns; the total amount of heat is the same in both cases, but in the decay the change takes so long that there is no appreciable change of temperature. A match gently rubbed in the dark appears luminous without flaming. Such changes as rusting and decay are termed *slow oxidation.* As distinguished from burning, *slow oxidation is the combination of a substance with oxygen without the accompaniment of noticeable light and heat.*

23. Kindling Temperature. — We know that some substances burn less easily than others; heat must be applied to cause them to *take fire* and continue to burn.

The kindling temperature of a substance is the lowest temperature at which it takes fire in air and continues to burn.

The kindling temperature varies with different substances; that of phosphorus is but little above the ordinary laboratory temperature, but the temperature produced by the burning is much higher. If the burning material is a good

conductor, iron for example, the heat is conducted away so rapidly that the temperature falls below the kindling temperature and the fire goes out. Similarly, gas lighted above an iron gauze (*a*, Fig. 10) does not catch fire below the gauze, because the heat of the flame is conducted away by the iron. The miner's safety lamp (Fig. 11) is based on this principle. By the invention of this device Sir Humphry Davy is to be credited with the saving of thousands of lives. When the material is in small pieces, or is powdered, there is more surface exposed to the oxygen of the air, so that the burning can proceed more rapidly. Finely divided iron will burn when sprinkled into a bunsen flame, since there is a large surface exposed, and there is no large mass to withdraw the heat. In the case of iron, the oxide produced is a solid which may cover the iron and prevent its coming in contact with the oxygen, thus stopping further action. Russia iron is artificially coated with a thin, regular film

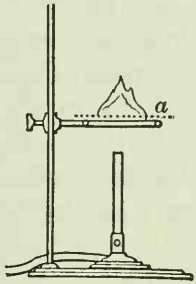

FIGURE 10.

The wire gauze conducts the heat so well that it is carried off sideways and dissipated into the air. Hence the gas below does not reach its kindling temperature.

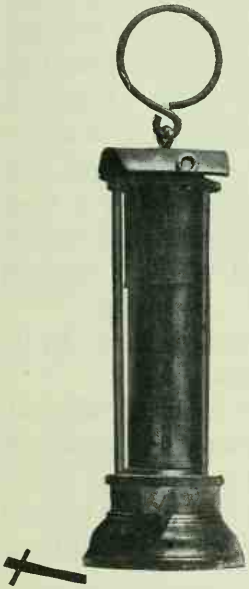

FIGURE 11. — THE MINER'S SAFETY LAMP.

The flame is surrounded by fine-mesh wire gauze which scatters heat so rapidly that the outside is always below the kindling temperature of the gas.

of *magnetic oxide of iron* (§ 431) to protect the sheet against rusting.

24. Spontaneous Combustion. — Linseed oil and other *drying oils* unite with oxygen and form a tough, resinous substance, the skin seen on the surface of paint that has been left exposed to the air. On painted surfaces, this skin holds the coloring matter and protects the material beneath. The heat generated in the slow oxidation of the linseed oil on a painted surface is dissipated into the air. If rags or waste soiled with such oils are left lying about, slow oxidation takes place. Since the rags are poor conductors, and their form prevents sufficient circulation of the air to keep them cool, the heat may accumulate until the stuff reaches its kindling temperature and it takes fire. Such cases of burning are said to be due to *spontaneous combustion.*

Spontaneous combustion is an active burning started by the accumulation of the heat of a slow oxidation.

Spontaneous combustion is liable to occur (1) when an easily oxidizable substance of low kindling temperature is exposed to the air, and (2) when conditions prevent the removal of heat. For these reasons, coal dust in coal bunkers sometimes becomes ignited, and a pile of damp hay may burst into flames.

25. The Bunsen Burner. — The bunsen burner was the first successful device for efficiently using gas for heating, and its principle is employed in all gas heaters. When the burner is in use, gas enters the barrel through the spud (Fig. 12), and mixes with a supply of air. The mixture rises to the top of the barrel, where it is ignited, drawing an additional supply of oxygen from the surrounding air. Atmospheric pressure forces air to enter the holes at the base of the barrel,

Robert Wilhelm Bunsen (1811–1899) was born in Göttingen and educated in its university. He served as professor in several German universities. At Heidelberg he had a career of nearly fifty years as a great teacher and brilliant investigator. His researches led to the acceptance of the idea of radicals existing in compounds. Many of his simple and efficient laboratory devices are in use to-day, notably the Bunsen burner. Bunsen may be regarded as the founder of modern gas analysis. His greatest work was the discovery, with Kirchhoff, of spectrum analysis. This proves useful in the detection of known elements, and has led to the discovery of new ones. By its means Bunsen found cæsium and rubidium.

because the gas as it issues from the spud at a high speed causes a partial vacuum in the barrel, and drags along particles of air with which it comes in contact.

The supply of gas entering the barrel is regulated by the gas cock, and the speed of the gas by varying the size of the opening in the spud. The supply of air is regulated by turning the collar so as to vary the size of the holes through which the air enters the barrel. If the gas pressure is low, the mixture of gas and air may burn downward more rapidly than it issues from the barrel. In this case the flame *strikes back* to the spud, where incomplete combustion takes place, causing a disagreeable odor. Sometimes the base becomes sufficiently hot to melt the rubber hose, and the escaping gas catches fire.

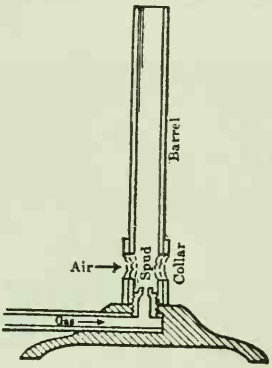

FIGURE 12.

Every cooking stove which uses gas has burners built on the principle of this laboratory device. It gives a clean rather than a sooty flame because the gas is mixed with a portion of air before it begins to burn.

FIGURE 13.

This shows where a test tube should be held to use the heat of the burner to best advantage. It also shows where to hold a substance which is to be oxidized.

The extreme tip of the outer flame is comparatively rich in oxygen and so causes many substances to oxidize when they are heated in it. Consequently, it is called the *oxidizing flame*. The portion of the flame having the *highest temperature* is just above the inner cone (Fig. 13).

The combustion in the bunsen flame is more rapid than that in the ordinary gas flame, since the fuel does not get far from the burner before burning. Therefore the flame is smaller and *for this reason* hotter. It is not luminous, owing to the rapid and complete burning and to the dilution of the materials by the nitrogen. In the laboratory, non-luminous flames are used chiefly because they do not deposit soot.

Courtesy of Popular Science Monthly.

FIGURE 14.

Air is so thin at high altitudes that aviators cannot breathe unless they are equipped with masks into which oxygen is led. The oxygen is carried in a compressed state in steel cylinders like those seen in drug stores.

26. Oxygen in Relation to Life. — All animals need oxygen for carrying on life processes. The air supplies this needed oxygen to land animals. Fishes breathe *dissolved* oxygen which water has absorbed from the air or which is liberated by green plants growing in the water. The oxygen taken in during the process of breathing is absorbed by the blood and carried to all parts of the body. The various tissues are slowly oxidized, heat being liberated by the action. It is this heat which keeps the bodies of the higher animals warmer than the surrounding air. One of the chief products of this oxidation is carbon dioxide, which is carried by the blood to the lungs and there exhaled.

Pure oxygen is sometimes administered in place of air to persons who are sick; this is done especially in cases of pneumonia, where the breathing area of the lungs has been reduced, and also in cases of asphyxiation. Aviators and mountain climbers who intend to reach high altitudes, where the air is highly rarefied, carry cylinders of compressed oxygen and breathing helmets to supply their need under the unusual conditions (Fig. 14). Firemen entering buildings filled with suffocating fumes, and rescue parties entering mines, are similarly equipped.

Plants feed on carbon dioxide, which they absorb from the air through their leaves. The carbon of this compound is retained in the tissues of the plants, but the oxygen for the most part is returned to the air. Thus plants and animals mutually assist in keeping the quantity of oxygen in the air constant. Plants, like animals, inhale a small quantity of oxygen directly from the air, and exhale a little carbon dioxide.

27. Other Uses of Oxygen. — Very high temperatures are obtained with the oxy-hydrogen (§ 39) and oxy-acetylene flames (§ 342). With the latter, steel rails and steel plates are joined by melting the ends together, and girders are cut through. Compressed oxygen for these purposes is sold in steel cylinders, where it is under high pressure. With the decrease in the price of compressed oxygen, increasing uses for this element have been found in industries requiring high temperatures for their operation. Cylinders of highly compressed oxygen are to be seen in nearly every automobile service station. Thousands of tons of " bottled " oxygen are used annually in this country.

28. Ozone. — A very interesting thing about oxygen is that it can exist in a second form. The name of this second

form is *ozone*. Ozone shows marked differences from ordinary oxygen. Silver, which is not affected by oxygen, is rapidly darkened (oxidized) by ozone. Rubber and many other organic materials are oxidized by ozone; a number of natural coloring matters are bleached by it; and disease germs are destroyed by contact with this active form of oxygen.

Ozone changes to oxygen readily at ordinary temperatures, and does not remain long in the air after its formation. Ordinary oxygen is the more *stable* or *durable* form. When electric sparks, or, better, silent electrical discharges, are passed through air or oxygen, the oxygen is changed into ozone. This gas has a strong and irritating odor which is often noticed in places where electrical machinery is working, particularly in electrical apparatus that uses high voltage. During thunderstorms, ozone is produced by electrical discharges through the air. In making ozone from oxygen a chemical change occurs, and *three* volumes of oxygen become *two* volumes of ozone. Hence ozone is heavier than oxygen.

Many attempts have been made to use ozone for the purification of air and water. Although there is no doubt as to the ability of ozone to kill germs and its power to remove objectionable odors, its practical use has not proved a success. Chlorine is better and cheaper.

29. Allotropism. — Oxygen and ozone are two forms of the same element and contain different amounts of energy. Such different forms of an element are termed *allotropic forms*. More striking examples of *allotropism* will be met in the study of phosphorus, sulphur, and carbon.

SUMMARY

Oxygen is prepared in the laboratory by:

(a) decomposition of mercuric oxide;

(b) decomposition of potassium or sodium chlorate in the presence of manganese doxide as a catalytic agent.

Commercially, oxygen is prepared:

(a) by the electrolysis of water;

(b) from liquid air.

Oxygen is 1.1 times as heavy as air. Liquid oxygen boils at $-182°$ and solidifies below $-227°$.

Oxygen **combines** with nearly all other elements. It is a very active element.

An **oxide** is a compound of oxygen and another element.

The combination of a substance with oxygen is called oxidation.

Combustion is any chemical action by which noticeable heat and light are evolved.

Ordinary burning is an oxidation accompanied by noticeable heat and light.

Slow oxidation is the combination of a substance with oxygen without the accompaniment of noticeable light or heat.

The **kindling temperature** of a substance is the lowest temperature at which it takes fire in air and continues to burn.

Spontaneous combustion is burning started by the accumulation of the heat of a slow oxidation.

A **catalyzer** is a material that changes the speed of chemical action without itself being permanently changed.

Ozone is a more active form of oxygen.

When elements are capable of existing in two or more forms, showing different properties, they are said to exist in **allotropic forms**, and to show the phenomena of **allotropism**.

EXERCISES

1. How would the production of oxygen be affected if potassium chlorate were heated without a catalytic agent?

2. How would you prove that water from a stream or a pond contains dissolved oxygen?

3. Name the product formed by burning each of the following: carbon, iron, sulphur, tin, magnesium, and phosphorus.

4. What is ordinary burning?

5. What would happen if a lighted candle were lowered into a jar of oxygen? Why?

6. Why does the throwing of a rug around a burning dress extinguish the flame?

7. Why should not the term *combustion* be applied to a case of slow oxidation?

8. Explain the successive use of paper, wood, and coal in making a coal fire.

9. Explain why polishing stoves prevents rusting.

10. Explain why a candle goes out if a wire gauze is slowly lowered till it touches the wick.

11. Why may a spark in a flour mill produce an explosion?

12. Give a practical illustration of putting out a fire (*a*) by lowering the temperature of the burning material below its kindling point; (*b*) by the removal of the combustible material; (*c*) by cutting off the supply of oxygen.

13. State the conditions necessary for spontaneous combustion.

14. Why are metal cans provided for the oily waste in woodturning shops?

15. Why should painters' rags not be thrown into a closet?

16. Name two gases in the air that are required by plants. Which in the larger amount?

17. Why is ozone used for the purification of water?

18. Why may blowing extinguish a candle?

19. Why may blowing on a fire make it burn more brightly?

20. In order to find the per cent of oxygen in air, the oxygen was absorbed by means of phosphorus, and the following data were obtained under like conditions: volume with oxygen, 99.8 c.c.; volume after oxygen has been removed, 78.9 c.c. Calculate the percent of oxygen.

CHAPTER III

HYDROGEN

30. Preparation by Electrolysis of Water. — If we dip the ends of the two wires from an electric battery into pure water, we find that practically no current passes. Water is a very poor conductor of electricity. If a small quantity of sulphuric acid is added to the water, the solution is a good conductor. During the passage of the current, bubbles form at the ends of the wires; at the positive electrode (*anode*) small bubbles of oxygen appear; at the negative electrode (*cathode*) there is a rapid evolution of hydrogen (Figs. 15, 16).

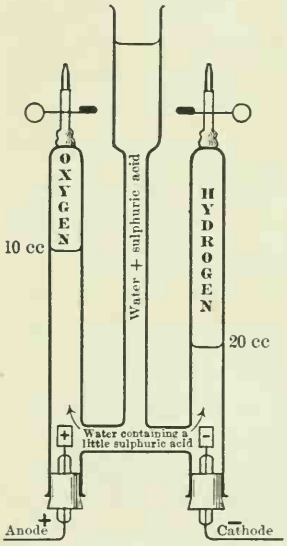

FIGURE 15.

An electric current passes between the two plates marked + and −, provided a little sulphuric acid is present. It is only water which is decomposed, for there is as much acid at the end of the operation as at the beginning.

If the gases are collected and their volumes compared, it will be found that twice as much hydrogen as oxygen has been set free. At the end of the experiment, although a little of the water has disappeared, the sulphuric acid is unchanged in amount. Sulphuric acid acts then in this case as a catalytic agent (§ 16). Other

catalytic agents might be used instead of the sulphuric acid, for example, potassium hydroxide, sodium hydroxide, or sodium sulphate. Commercially, with large iron apparatus, potassium hydroxide is used.

A part of the water is converted by electrolysis into the gases oxygen and hydrogen, and the volumes of these gases are very large compared with the bulk of the water which is decomposed.

The chemical change may be represented briefly by the word equation:

water ⟶ hydrogen + oxygen

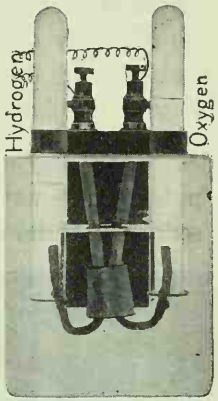

FIGURE 16.

Another form of apparatus for separating water into its elements by the use of the electric current. This is less easily broken than the one shown in Figure 15.

31. Action of Metals on Water.— Potassium and sodium are metallic elements which are very active chemically. When a piece of potassium is placed on water it skims back and forth, giving decided evidence of a violent reaction. If a large piece of the metal is used, the experiment may prove dangerous. The element seems to take fire, but in reality the flame is due chiefly to the hydrogen which is set free from the water and which becomes ignited from the heat of the reaction.

When a small piece of sodium is used, although the action is very rapid, the heat generated is not usually sufficient to ignite the hydrogen. The temperature may become high enough to set fire to the hydrogen if the water is warm, or if the sodium cannot move about freely on the surface of the water. Figure 17 shows an arrangement with which the

hydrogen, set free by the action of sodium with water, can be burned safely.

In each of these reactions of metals with water, the metal sets free only one half of the hydrogen of the water, and combines with the remaining half and with all of the oxygen, to form the *hydroxide* of the metal. The following word equations may be used to represent the reactions:

potassium + water ⟶ potassium hydroxide + hydrogen
sodium + water ⟶ sodium hydroxide + hydrogen

FIGURE 17.

Sodium has been dropped down the open tube. The hydrogen which is being liberated is burning at the upper end of the tube.

The potassium hydroxide, or the sodium hydroxide, dissolves in the water left in the vessel. Some other metals will also react with water. When calcium is used, the action is quiet, and not all of the calcium hydroxide dissolves, so we obtain a cloudy liquid. Magnesium will react only when the water is hot.

If steam is passed through a heated pipe filled with small iron nails, an abundant supply of hydrogen can be obtained. The oxygen of the steam combines with the iron, according to the equation:

iron + water (steam) ⟶ iron oxide + hydrogen

32. Replacement in Acids by Metals. — In the sixteenth century, Paracelsus observed that when iron dissolved in an acid a gas was evolved. All acids contain hydrogen that can be exchanged for a metal, and in a number of cases the hydrogen is liberated and can be obtained free. The

most convenient method of preparing small quantities of hydrogen is to add a water solution of sulphuric acid to zinc (Fig. 18). The reaction takes place at ordinary temperatures and can be controlled easily. While hydrogen is set free during the reaction, the zinc combines with the remaining part of the sulphuric acid and forms a new compound, zinc sulphate, which remains dissolved in the liquid in the generator:

$$\underset{\{\text{hydrogen, sulphur, oxygen}}{\text{sulphuric acid}} + \text{zinc} \longrightarrow \underset{\{\text{zinc, sulphur, oxygen}}{\text{zinc sulphate}} + \text{hydrogen}$$

Sulphuric acid and zinc sulphate are compounds, and the words printed in small letters under each of these names indicate of what elements that compound is composed.

How fast the action will proceed will depend on several factors: the temperature, the concentration of the acid solution, the surface of the metal that is exposed, the purity of the metal and acid, and the amount of zinc sulphate that has been formed during the reaction. The ordinary concentrated sulphuric acid should be diluted with from four to six times its volume of water. A catalytic agent, for example carbon or copper, must be in contact with the zinc. Commercial zinc generally has sufficient impurities to give good results.

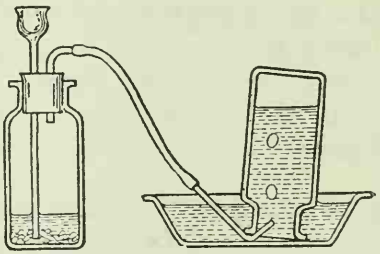

FIGURE 18.

Hydrogen is liberated when zinc reacts with dilute sulphuric acid. No heat is needed. The gas is collected in the same way as oxygen, for neither of these gases is very soluble in water. Zinc sulphate is also formed, but it is not seen because it dissolves in the water contained in the dilute sulphuric acid.

Other metals besides zinc and other acids besides sulphuric acid may be used for the preparation of hydrogen, but it is not true that free hydrogen can be obtained by the reaction between *any* acid and *any* metal. Dilute solutions of either sulphuric or hydrochloric acid are usually employed, with either zinc or iron.

33. Physical Properties. — Hydrogen is a gas without color, taste, or odor. When commercial zinc and acid are used in its preparation, impurities are carried along with the hydrogen, and give it a peculiar, disagreeable odor. If iron is used instead of zinc, the unpleasantness of the odor is more noticeable. Hydrogen is scarcely soluble in water. It is the lightest substance known; *1 liter of hydrogen weighs 0.09 of a gram.*

Hydrogen has been liquefied and solidified. The liquid is one fourteenth as dense as water, and is the lightest liquid known.

34. Occlusion. — Platinum and some other metals have the power of condensing (*adsorbing*) large volumes of hydrogen on their surfaces. The hydrogen is expelled when the metal is warmed. Such an adsorption of gas by a solid is called *occlusion*. While the gas is being adsorbed, considerable heat is set free, and, if oxygen is present, the hydrogen may ignite. The occluding action of such a metal is utilized in self-lighting gas burners and cigar lighters.

Chemical Properties

35. Combustibility. — The most important chemical property of hydrogen is its combustibility. Cavendish, in 1783, showed that water is formed when hydrogen burns in the air.

The water formed by the combustion of hydrogen usually passes off unnoticed as steam, but it may be condensed on a cool surface (Fig. 19). The flame of hydrogen is blue, almost

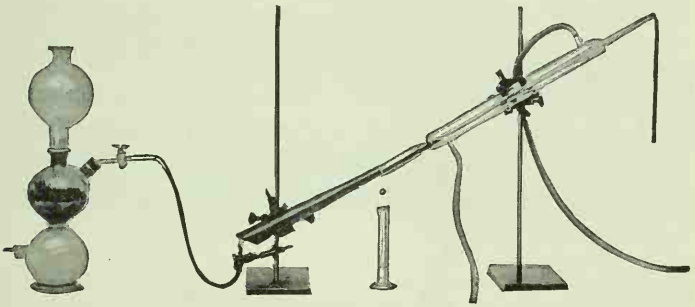

FIGURE 19.

Hydrogen from the generator burns below the mouth of a metal tube. The steam that is formed is turned into water as it passes through the condenser.

invisible in the daylight, and is very hot. Hydrogen in burning gives as much heat as over four times its *weight* of coal.

If hydrogen and oxygen are mixed, and the mixture is raised to its kindling temperature, or if an electric spark is passed through the mixture, combustion takes place throughout the entire mass almost instantaneously, producing a sudden increase in volume. Such a rapid combustion, accompanied by a sudden increase in pressure, is termed an *explosion*.

36. Combustible and Supporter of Combustion Interchangeable.—We have seen that hydrogen burns with a pale-blue flame in air. Similarly, a jet of air or oxygen can be made to burn in hydrogen. This illustrates the facts that *the combustible substance and the supporter of combustion are interchangeable, and that the terms are relative.*

37. Deoxidizing Action. — Hydrogen will take oxygen from many oxides when they are heated in it (Fig. 20), forming water (steam) and leaving the metal free:

$$\text{copper oxide} + \text{hydrogen} \longrightarrow \text{water} + \text{copper}$$

In this reaction, the oxygen was removed from the copper oxide and the metal obtained. This deoxidizing action is called a reduction, so that it is often said that *reduction is*

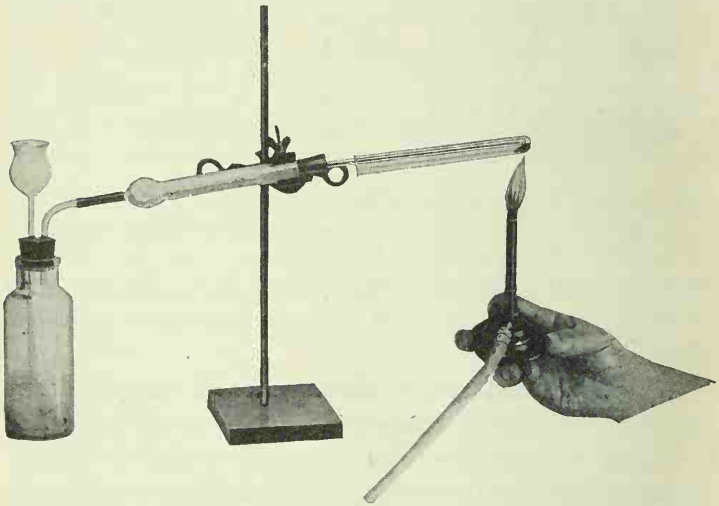

FIGURE 20.

Hydrogen is generated, dried by passing through a bulb tube which contains calcium chloride, and then is led into a test tube where copper oxide is being heated. The hydrogen takes oxygen from the oxide and copper is left. The water thus formed collects in the cool part of the test tube.

the process of taking away oxygen from a substance. Substances that take oxygen from compounds are called *deoxidizing* (*reducing*) *agents.* In the reaction with copper oxide, hydrogen was used as a deoxidizing agent.

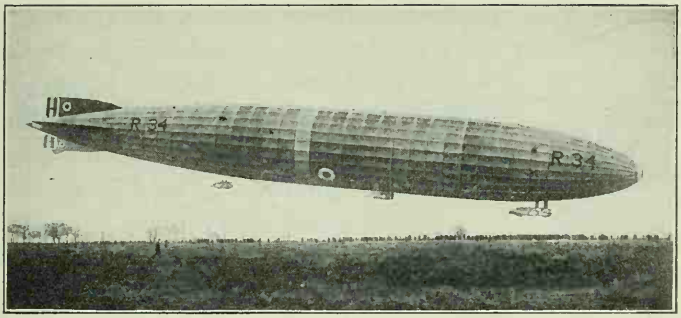

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FIGURE 21.

The R 34 about to alight after her flight across the Atlantic. The huge body is filled with hydrogen, less than one fourteenth as heavy as air.

Oxidation and deoxidation always go on together. In this case, while copper oxide was being deoxidized, hydrogen was being oxidized. Hydrogen is one of the most energetic deoxidizing agents.

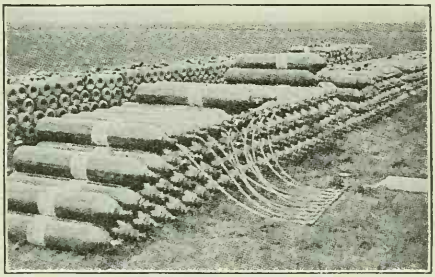


FIGURE 22.

Steel bottles filled with compressed hydrogen ready to refill the R 34 for her return flight across the ocean. The picture shows how gases are stored and transported, and gives an idea of the enormous amount of hydrogen needed for a dirigible.

38. Uses. — Hydrogen in burning produces much heat, and it is therefore used in gaseous fuels. *Water gas* is made by blowing steam into a mass of white-hot coal or coke. Hydrogen is produced together with an equal volume of carbon monoxide. Both of these gases will burn and the mixture is suitable for heating, but neither gas

gives much light. Nearly three fourths of the gas used in homes is water gas which has been made better for heating and lighting purposes (§ 340), by the addition of petroleum products.

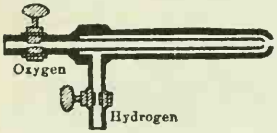


FIGURE 23.

The oxyhydrogen blowpipe gives much higher temperatures than can be obtained from ordinary illuminating gas. Notice that the gases do not mix before reaching the flame, and that the oxygen is fed through the *inside* tube.

Because hydrogen is the lightest gas known it is used in airships. One part of hydrogen is capable of raising 13.4 times its weight of balloon equipment (Fig. 21). Although helium is somewhat heavier than hydrogen, it is preferred to hydrogen for airships, because it will not burn.

39. Oxyhydrogen Blowpipe. — The oxyhydrogen blowpipe makes available the high temperature of the hydrogen flame. This blowpipe consists of two tubes (Fig. 23). The hydrogen is supplied through the outer tube and lighted at the tip; then the oxygen is turned on. The gases are supplied under pressure and give an intense heat. Such a blast flame is used to melt platinum and other materials difficult to melt, such as aluminum oxide in the manufacture of artificial rubies.

Figure 24 shows a blowpipe constructed on the principle of the oxyhydrogen blowpipe, using ordinary illuminating gas and air.

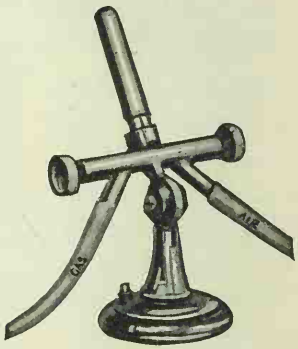


FIGURE 24.

A blowpipe that is constructed like the oxyhydrogen blowpipe. It uses illuminating gas instead of hydrogen, and does not produce so high a temperature.

The cleanliness of the flame, as well as the temperature, is useful in the process of *lead burning*. Pieces of lead, having been placed in the positions desired, are melted at the edges by the use of a hydrogen flame so that they join together.

40. Hydrogen Hardens Oils. — A very important use for hydrogen is in the treatment of certain oils in order to produce harder fats. For instance, cotton seed oil will react and combine with a small amount of hydrogen in the presence of metallic nickel, which acts as a catalytic agent. The resulting compound is like tallow, somewhat hard. Such hard fats are useful in cooking compounds, in substitutes for butter, and for soapmaking. The operation of combining the fat with hydrogen is sometimes called *hydrogenation*, but more commonly the fat is merely said to be hardened.

SUMMARY

Hydrogen is commonly prepared by:

(1) the electrolysis of water (commercial method);

(2) the reaction between water and a metal;

(3) replacement in an acid by a metal. This is the most convenient laboratory method.

A liter of hydrogen, under standard conditions, weighs 0.09 gram. A liter of water at 20° dissolves 18.2 c.c. of hydrogen. Liquid hydrogen boils at — 252.5° and solidifies at — 259°.

Hydrogen **burns** in oxygen or in air, forming water. It is a powerful **deoxidizing agent.** The chief **uses** of hydrogen are for fuel, for balloons, and for the hardening of oils.

EXERCISES

1. What would be the result of collecting together the gases formed by the electrolysis of water and applying a flame to the mixture?

2. Would you use water or sand to extinguish burning sodium? Why?

3. Would you use zinc or iron for making hydrogen to fill a large balloon? Why?

4. Why is hydrogen generally used in airships? What objection is there to its use?

5. What becomes of the product, other than hydrogen, which is formed when zinc and sulphuric acid react?

6. Is water an oxide?

7. How would a soap bubble behave if filled with hydrogen instead of with air?

8. Would a bottle of hydrogen remain full if left inverted overnight with its mouth under water? Why?

9. Why should all the air be expelled from a hydrogen generator before the gas is lighted at the end of the delivery tube?

10. Should vessels containing hydrogen be kept mouth upward or mouth downward? Why?

11. Why would pure hydrogen not make an illuminating gas?

12. Could hydrogen be substituted for illuminating gas in an ordinary gas stove?

13. What is formed when iron oxide is heated in a current of hydrogen?

14. Would a Welsbach burner supplied with hydrogen give light?

15. Why is hydrogen called a deoxidizing agent?

16. What is lead burning? On what two properties of hydrogen does it depend?

17. By making use of hydrogen, how could you show that air contains oxygen?

18. Mention two ways in which the cheap production of hydrogen tends to decrease the cost of living.

CHAPTER IV

WATER AND SOLUTION

41. Analysis and Synthesis. — In the electrolysis of water, we showed that water could be separated into two volumes of hydrogen and one volume of oxygen. Such a separation is called an *analysis*. The combining of these substances to produce water is called a *synthesis* of water.

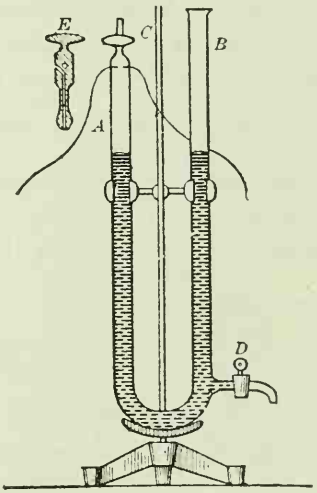


FIGURE 25.

An experiment performed in this apparatus shows that 2 volumes of hydrogen unite with 1 volume of oxygen.

42. Synthesis by Volume. — If known volumes of hydrogen and oxygen are introduced into a tube inverted over mercury, and exploded by an electric spark between platinum wires fused through the glass, it is found that the volumes of the gases uniting are in the ratio of two volumes of hydrogen to one of oxygen, and that any excess of either gas is left unchanged. It is only when two volumes of hydrogen are mixed with one of oxygen that the two gases totally disappear. A little mist is seen on the tube, which is the moisture formed, and the mercury rises and fills the tube. This, again, shows

that water consists of two volumes of hydrogen and one of oxygen. Another form of apparatus (Fig. 25), differing in the shape of the tube from that just described, facilitates the adjustment and reading of the mercury levels. Additional mercury, if needed, can be poured through the open arm *B*, and an excess can be drawn off through the lower stopcock *D*. The gases used in *A* can be drawn in easily through the threeway stopcock *C*, shown in detail at *E*. If the tube *A* is provided with a heating device so that the temperature can be raised above 100° C., the volume of the steam can be measured. If the measurements are made at the same temperature and pressure, it will be found that *the volume of the steam is equal to the volume of the hydrogen.*

2 volumes hydrogen + 1 volume oxygen $\longrightarrow$ 2 volumes steam

43. Synthesis by Weight. — If dry hydrogen is passed over a weighed quantity of copper oxide which is heated, steam and copper result (Fig. 26). The water can be col-

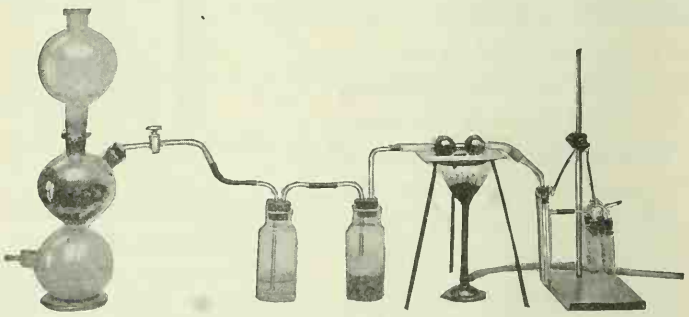


FIGURE 26.

The two-bulb tube loses weight in this experiment because the copper oxide it contains is reduced by hydrogen. The apparatus at the end gains in weight because all the water formed is collected there. The weight of the water minus the weight of the oxygen lost by the copper oxide is the weight of the hydrogen used.

lected and weighed in a tube containing a drying agent. The weight lost by the copper oxide is the weight of the oxygen. The difference between the weight of the oxygen and the weight of the water formed is the weight of the hydrogen.

44. Law of Definite Proportions. — The ratio between the weights of the oxygen and hydrogen in water is found to be 7.94 : 1. Wherever water is found and however it is made, it always contains 7.94 times as much oxygen as hydrogen by weight. This relation is unvarying. Experience has shown that *every compound has a definite composition by weight.* This is known as the *law of definite proportions.*

45. Physical Properties of Water. — Pure water is an odorless liquid. Small quantities appear to be colorless, although large masses show a distinct blue color. Water is usually taken as the standard in comparisons of physical properties of liquids and solids. The zero of the Centigrade thermometer registers the position of the top of the mercury column when the thermometer is placed in melting ice, and since a pure substance on being warmed always melts at the same temperature as that at which it would solidify if cooled, the zero of the Centigrade thermometer is the freezing point for water.

When pure water is heated to 100° C. under a pressure of 760 mm., it boils; if we continue to apply heat, the temperature does not rise higher, provided the steam is allowed to escape. The heat used in converting water into steam is known as the *heat of vaporization,* or the latent heat of steam; it is given off when the steam condenses. The heat used in changing ice to water is known as the *heat of fusion.* This is also latent heat, as it is given off when the water changes back to ice.

These quantities of heat are commonly measured in units known as *calories*. The calorie is the quantity of heat required to raise the temperature of a gram of water 1° Centigrade. About 80 calories are required to change a gram of

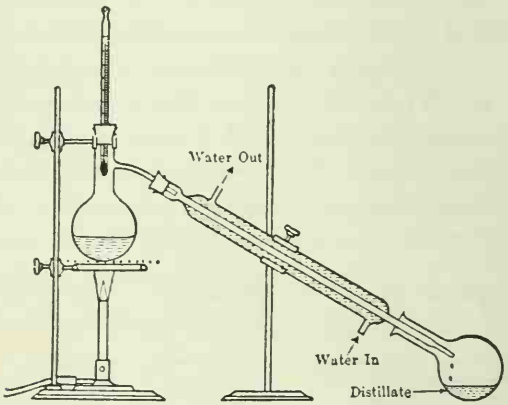


FIGURE 27.

Steam passes through a tube that is surrounded by a stream of cold water, and is thus condensed again to water. Any solid non-volatile impurities are left in the flask.

ice at 0° C. to water at 0° C., and about 540 calories are required to change the same mass of water at 100° C. to steam at 100° C.

Both the freezing and the boiling temperatures change when the pressure changes; increased pressure raises the boiling point and lowers the freezing point, in both cases tending to keep the substance in the *liquid* form. Any dissolved solid acts in the same way.

Water requires a greater quantity of heat to raise its temperature than do most substances, so that its temperature changes more slowly than that of most objects. Therefore oceans and large lakes considerably affect the climate of the neighboring land.

46. Distillation. — All natural water contains dissolved substances. It is therefore necessary to boil water and then condense the steam to make it fit for chemical use; this process is called *distillation* (Figs. 27 and 28). Solids and

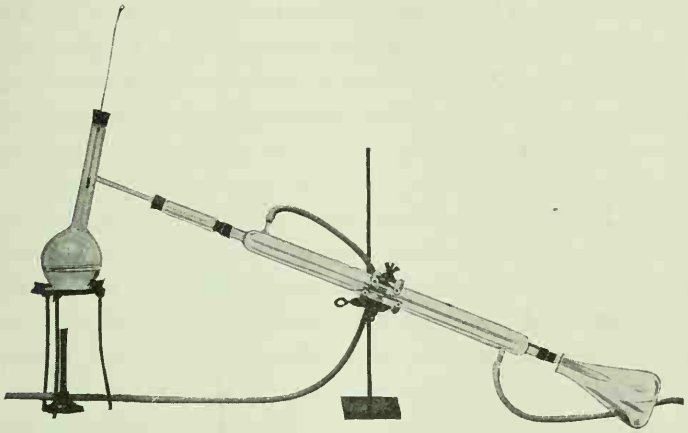


FIGURE 28.

A photograph of a distilling apparatus like that shown in Figure 27.

liquids with boiling points much higher than that of water are left behind, as the temperature of pure steam remains the same during the distillation. Materials having lower boiling points than water are distilled before or with the water; such impurities, ammonia for example, are found in the first portion of the condensed steam, and this is rejected.

Distillation consists in changing a liquid to a gas (vaporization), *then cooling the gas so that it becomes a liquid again* (condensation), *and collecting the distillate in a separate vessel.*

47. Steam. — Steam is water in the gaseous state; at ordinary pressure it condenses to liquid at 100° C.; if the

pressure be lessened, it remains in the gaseous condition at lower temperatures. The volume of steam is about 1700 times that of the water from which it was formed.

48. Ice. — If its temperature is lowered to 0° C. and energy is removed, water solidifies to ice, usually crystallizing in hexagonal clusters of needles. There is considerable expansion during the solidification, and consequently ice is lighter than water.

49. Solution. — An important property of water is its ability to dissolve a large number of substances. A substance is said to be in *solution* in a liquid when it is distributed uniformly through the liquid in a state of such fine division that its particles cannot be seen and do not separate on standing. When the particles are visible, the substance is said to be in *suspension*, and will usually settle quickly. *A solution is a uniform mixture that does not follow the law of definite proportions.* A liquid used to dissolve a substance is called a *solvent*. The dissolved substance is termed the *solute*. A solution will not boil at the same temperature as the solvent, nor will their freezing points be the same.

Alcohol and water, or glycerine and water, form uniform mixtures when brought together. Liquids that dissolve in each other in all proportions are said to be *miscible*. Kerosene and water are *non-miscible* liquids, since they separate on standing.

50. Saturation. — A solution is not a definite compound. A small portion of salt may be dissolved in a large quantity of water; such a solution is said to be *dilute*. In a dilute

solution, the substance is as uniformly distributed in all parts of the liquid as it is in one containing a much larger proportion of the dissolved substance. A definite amount of water will dissolve any amount of a given solid up to a fixed quantity. If a liter of water at 20° C. is taken, it is possible to dissolve in it any weight of salt up to 360 grams. When the water has dissolved all the salt it can at a given temperature it is said to be *saturated* with salt at the temperature mentioned. A similar statement may be made concerning the solubility of any solid in any liquid. When any solvent has dissolved all of a given solute that it can without changing the conditions of the experiment, it is said to be *saturated with respect to that substance under the existing conditions.* A solution saturated with one substance may dissolve other substances. Thus, water saturated with salt can dissolve saltpeter.

51. Relation of Solubility to Temperature. — The solubility of most substances is decidedly affected by the temperature. Solids are usually, *but not always,* more soluble in liquids at high

FIGURE 29.

Sodium nitrate is much more soluble in hot than in cold water. The smaller pile would dissolve in the water in the graduate if cold, and the larger if the water were hot.

than at low temperatures. Sugar, alum, and saltpeter (Fig. 29) are more soluble in hot water than in cold. Salt dissolves nearly as well in cold as in hot water (Fig. 30).

Calcium hydroxide, used in the preparation of limewater, is more soluble in cold water than in warm.

Unlike solids, the solubility of gases in liquids decreases as the temperature rises. Ammonia and carbon dioxide are less soluble in hot water than they are in cold. Different substances differ very much in their solubility in a given solvent, and different solvents differ in their power to dissolve the same substance.

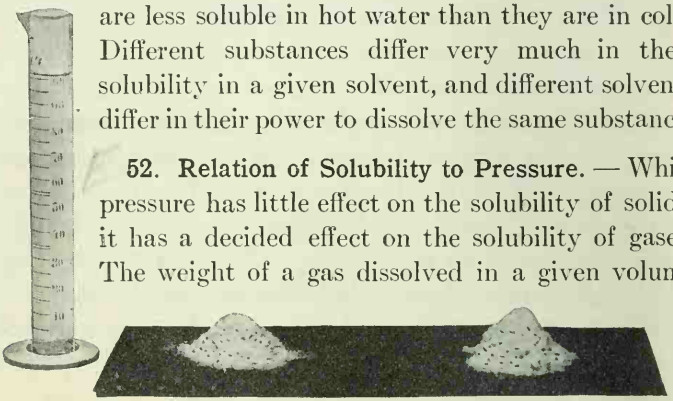


FIGURE 30.

Common salt is only slightly more soluble in boiling water than it is in cold water. The pile on the right is the amount that will dissolve in the water in the graduate if the water is hot.

52. Relation of Solubility to Pressure. — While pressure has little effect on the solubility of solids, it has a decided effect on the solubility of gases. The weight of a gas dissolved in a given volume of a liquid is directly proportional to the pressure. Soda water is usually charged with carbon dioxide under a pressure of ten atmospheres. The weight of the carbon dioxide dissolved is ten times as great as would be dissolved under ordinary air pressure.

53. Freezing Mixtures. — There are important energy changes during solution. When a solid is dissolved, energy is absorbed and there is generally a fall in temperature. When ice and salt are mixed, some of the ice melts and the salt dissolves in the water. Both processes result in the absorption of heat, and the temperature of the mixture falls considerably below the freezing point of pure water.

The salt water does not freeze because the freezing point of salt water is lower than that of pure water. When equal parts of ammonium nitrate and water are mixed at 0° C., the temperature falls to − 15° C. In the freezing of ice cream, the heat necessary to melt the ice and dissolve the salt is mainly taken from the inner can and its contents.

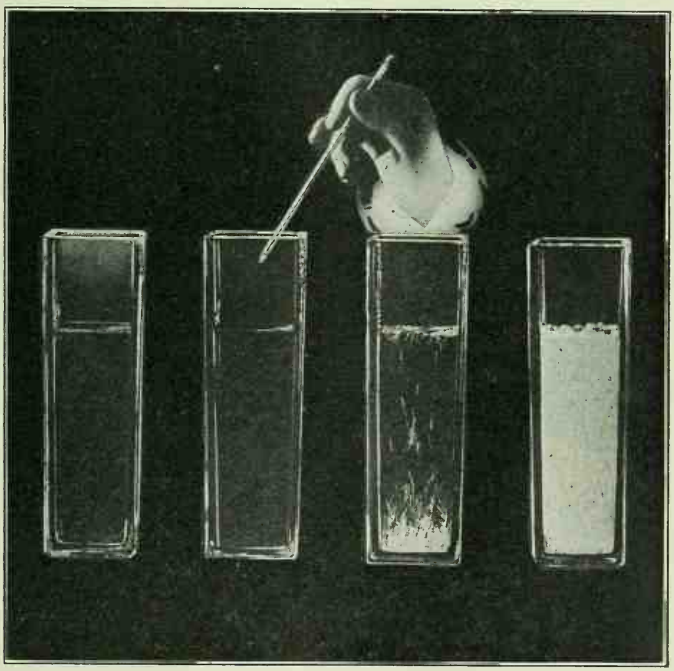


FIGURE 31.

The first jar contains a supersaturated solution of hypo. Into the second a minute crystal of hypo is being dropped. The third and fourth jars show the rapid crystallization that immediately sets in.

54. Supersaturation. — A *supersaturated solution* of a solid represents an abnormal condition in which more of the

solute is held in solution than is held in the saturated solution of the same temperature. Such solutions are usually made by preparing saturated solutions at a high temperature and then allowing them to cool without disturbance or contact with any of the solid form of the solute. Whether the solution is unsaturated, saturated, or supersaturated can be told by adding a particle of the solute. If the particle dissolves, the solution is unsaturated; if the particle remains unchanged, the solution is saturated; if a rapid crystallization sets in (Fig. 31) accompanied by the evolution of heat, the solution is supersaturated.

Supersaturated solutions of gases are made by exerting pressure on the gas that is in contact with water. When the pressure is removed, the dissolved gas does not immediately leave the solution; agitation of the liquid, or the introduction of gas bubbles, causes a quick liberation of the dissolved gas.

FIGURE 32.

These crystals of alum have grown into each other as they were slowly formed from a solution. A single one of them, if well developed, would look like Figure 33. Alum crystals contain a large amount of water of crystallization (water of hydration).

55. Crystals. — The fact that the solubility varies with the temperature is made use of in separating solids from solution. If a solution that is saturated at a high temperature be allowed to cool slowly, the dissolved substance will often separate into definite geometrical forms called *crystals*. Crystals may be obtained from the dilute solution of a solid by the evaporation of the solvent. Crystals (Figs. 32 to 35) are symmetrical and often trans-

parent. Recent work with X-rays indicates a definite arrangement of the particles of the elements within the crystal.

56. Water of Crystallization. — Many substances in crystallizing from aqueous solutions unite with a definite quantity of water which is necessary to the shape of the crystal. This water is called *water of crystallization*. Copper sulphate or blue vitriol contains water of crystallization, and if it is heated in a test tube, moisture will be seen on the cooler portions of the tube, and the blue crystal will change to a white powder. The heating has driven off the water of crystallization.

FIGURE 33.

This shows only one side of a crystal of chrome alum. The other is exactly the same; so its form is something like that of two pyramids put base to base.

FIGURE 34.

A piece of "rock salt." This natural fragment indicates the cubical nature of the crystal. It does not contain water of crystallization.

Substances like blue vitriol (Fig. 35) and crystallized zinc sulphate, formed by the union of a chemical compound with a definite amount of water, are often termed *hydrates*. Water of crystallization is sometimes called *water of hydration*.

57. Efflorescence. — If a crystal of washing soda is exposed to the air in a dry place, it will lose its water of crystallization and become covered with a fine powder. Such a material is said to be *efflorescent*. An *efflorescent*

substance is one that loses water of crystallization on exposure to the air.

FIGURE 35.

A mass of blue vitriol (copper sulphate) crystals. They are so intermingled that it is difficult to distinguish the definite shape they all have. A crystal of any kind is bounded by planes, never by curved surfaces, and all the angles formed by the planes of a given substance are definite ones.

58. Hygroscopic and Deliquescent Substances. — Many materials, as lime, wool, and silk, usually absorb moisture from the air and are therefore said to be *hygroscopic*. Calcium chloride and caustic potash absorb sufficient moisture to dissolve them or to cause them to become *wet*, and are said to be *deliquescent*. Such materials are useful as drying agents. Whether a substance will give up its water of crystallization to the air or will absorb moisture from the air depends largely on the amount of moisture already in the air and also on the temperature and on the nature of the substance. A *hygroscopic substance* is one that will absorb moisture from the air. A *deliquescent substance* is one that absorbs enough moisture from the air to become wet.

HYDROGEN PEROXIDE

59. Composition. — Hydrogen and oxygen form two different compounds: *water*, which contains 8 times as much

oxygen as hydrogen by weight; and *hydrogen peroxide*, which contains 16 times as much oxygen as hydrogen. The prefix *per-* in the name means that this compound is richer in oxygen. The substance is sometimes called *hydrogen dioxide*, because it contains twice as much oxygen in comparison with a given weight of hydrogen as water does.

60. Preparation. — Hydrogen peroxide is prepared by the action of barium peroxide with dilute acids. Commercially, the barium peroxide is mixed with water to the consistency of cream. This mixture is then added to a dilute solution of sulphuric acid or phosphoric acid, care being taken to keep the temperature below 15° C.:

$$\text{barium peroxide} + \text{sulphuric acid} \longrightarrow \text{barium sulphate} + \text{hydrogen peroxide}$$

The precipitate of barium sulphate or of barium phosphate is allowed to settle and the solution of hydrogen peroxide is decanted, or drawn off.

The commercial form of hydrogen peroxide is its 3% solution. The mark "10 v" means that it will yield a volume of oxygen equal to 10 times that of the solution. To prevent the peroxide from decomposition, the solution is kept slightly acid or a very small quantity of acetanilid is sometimes added. Hydrogen peroxide is sold under various trade names.

61. Properties. — Hydrogen peroxide itself is a clear, syrupy liquid about $1\frac{1}{2}$ times as dense as water, with which it is miscible. Pure hydrogen peroxide decomposes with explosive violence. Even in the dilute 3% water solution, the decomposition proceeds slowly according to the equation:

$$\text{hydrogen peroxide} \longrightarrow \text{water} + \text{oxygen}$$

62. Uses. — Hydrogen peroxide is used as a bleaching and disinfecting agent. Wool, silk, feathers, hair, and ivory are bleached by the oxidation of their coloring matters. Harmful bacteria and decomposing matter are destroyed by it; hence its occasional use as an antiseptic for superficial wounds and sores. It is, however, somewhat irritating to exposed flesh and to the mucous membrane.

63. Law of Multiple Proportions. — In water, the weights of the hydrogen and oxygen are in the ratio of 1 to 8. In hydrogen peroxide, the ratio is 1 to 16. Thus the hydrogen in the peroxide is combined with twice as much oxygen as the hydrogen of the water. A similar relation is found in many cases. *In a series of compounds that are made up of the same elements, a simple ratio exists between the weights of any one element that combine with a fixed weight of another element.* This ratio may be expressed by small whole numbers. This is known as the *law of multiple proportions* or Dalton's second law.

SUMMARY

The composition of water can be shown by **analysis** and by **synthesis.** The synthesis of water is the combining of hydrogen and oxygen to form water. Two volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

Water consists of 1 part by weight of hydrogen combined with 8 parts of oxygen; and, since it always has this composition, it illustrates the **law of definite proportions**, which states that every compound has a definite composition by weight.

Water is the standard for the specific gravity of liquids and solids. Its freezing point and its boiling point are respectively 0° and 100° on the Centigrade thermometer scale.

Water can be purified by distillation.

A **solution** is a uniform mixture that does not conform to the law of definite proportions.

Water is the most common **solvent.** The amount of a solute in a given quantity of a solvent causes a solution to be either unsaturated, saturated, or supersaturated. Important temperature changes take place during solution.

A **hygroscopic** substance is one that will absorb moisture from the air. If the substance absorbs enough moisture to become wet, it is said to be **deliquescent.**

An **efflorescent** substance is one that loses water of crystallization on exposure to the air.

Water of crystallization is the definite amount of water with which some substances combine when they separate as crystals from a water solution.

Hydrogen peroxide can be prepared by the addition of barium peroxide to cold dilute acids, as phosphoric acid, sulphuric acid, or hydrochloric acid. Hydrogen peroxide is a strong oxidizing agent and is used as a germicide and for bleaching.

Hydrogen peroxide consists of 1 part by weight of hydrogen combined with 16 parts by weight of oxygen.

The composition of water and of hydrogen dioxide illustrates the **law of multiple proportions**, which is stated thus: In a series of compounds that are made up of the same elements, a simple ratio exists between the weights of any one element that combine with a fixed weight of another element.

EXERCISES

1. When sugar is heated sufficiently to char it, water is driven off. What two elements besides carbon must sugar contain?

2. Why does a thin film of water collect on the inside of a lamp chimney when the lamp is first lighted? Why does the moisture soon disappear?

3. Dry hydrogen was passed over heated copper oxide and the water formed was absorbed by fused calcium chloride. The following results were obtained:

Weight of copper oxide tube before experiment . .	70 g.
Weight of copper oxide tube after experiment . . .	66 g.
Weight of calcium chloride tube after experiment . .	106.5 g.
Weight of calcium chloride tube before experiment .	102 g.

From the above data calculate the weight composition of water.

4. 15 c.c. of oxygen were collected in a eudiometer (gas measuring tube) over mercury. Dry hydrogen was passed into the eudiometer until the volume of the mixed gas was 22.4 c.c. A spark was then passed through the mixture. What gas was left in the eudiometer? How would you prove your answer? What would be the volume of the remaining gas?

5. Mention three ways by which water can be decomposed.

6. Describe an experiment that you could perform to illustrate the law of definite proportions.

7. What does the analysis of water show its composition to be by volume?

8. Mention two methods for the synthesis of water.

9. What physical properties of water determine the fixed points on a Centigrade thermometer?

10. Why does water put out fire?

11. How can drinking water be made from salt water?

12. How does a solution differ from a chemical compound?

13. What is the chemical statement of the old saying: "Oil and water will not mix"?

14. Distinguish between *solvent* and *solute*.

15. Water is saturated with washing soda at a high temperature and the solution is allowed to cool. Would the solution then be saturated?

16. How could you determine whether a certain solution is saturated, unsaturated, or supersaturated?

17. How could a supersaturated solution of "hypo" be prepared?

18. When sea water is evaporated, why does one of the substances in solution begin to separate before the others?

19. How would you show that any natural water is a dilute solution?

20. Is ammonia more soluble in cold or in hot water? Why?

21. Why does the solution from a soda fountain bubble so freely?

22. Why are salt and ice used in ice cream freezers?

23. How could you obtain crystals of washing soda from the dry powder?

24. Distinguish between a hygroscopic and a deliquescent substance. Give an example of each.

25. Why do crystals of washing soda become covered with a coating of white powder when exposed to the air?

26. Why is fused calcium chloride used as a drying agent?

27. There are five oxides of nitrogen in which the weights of oxygen and nitrogen are respectively in the ratios: 16 : 28, 32 : 28, 48 : 28, 64 : 28, and 80 : 28. Show how the composition of these compounds illustrates the law of multiple proportions.

28. Mention three ways by which water can be purified.

29. How does the composition of water illustrate the law of definite proportions?

30. Why does not a solution of hydrogen peroxide keep well when exposed to the air?

31. If sold at the same price per pound, would it be more economical to buy washing soda before or after it has been exposed to the air for some time?

CHAPTER V

ATOMS AND MOLECULES

64. Science Uses Imagination. — The human body is a wonderful instrument, but we are not able to detect everything which exists and happens. We aid our senses by microscopes, telescopes, and other devices. But, even with such help, there are multitudes of things which will never be observed directly by any human being.

It is often the unseen things which affect our lives very seriously. We cannot observe electricity gathering in the clouds; but lightning burns houses and sometimes kills people. No one has yet seen the germs causing certain diseases. That such organisms do exist, however, is believed by medical men, for they know that these diseases are contagious and that they can spread only by means of germs.

Science is based largely on the idea that the more we know and understand, the more safely and happily we shall live. Hence a scientist realizes that it is necessary to use the imagination in order to find out what we can, even about things too small or too far away to be seen.

65. Guesses Help Us to Understand. — Experience has proved that one way to get useful knowledge is to watch effects and then make careful guesses about their causes. If later experience shows that the guess helps us to make successful predictions about what is going to happen, we may reasonably conclude that the guess had some truth in it.

If predictions fail, then we conclude that the guess was wrong and we try to make a better one. Some of the scientific guesses about unseen things have stood the tests of many years.

66. Theories. — An *hypothesis*, or a *theory*, is a guess based on all the facts that can be found, which has proved reliable in making predictions or new discoveries.

To get theories scientists must use imagination. But they must check carefully by many tests and observations whatever they reason out in this way. They use experiments not only to discover facts for direct use, but also to regulate and control the imagination necessary to understand things which cannot be seen directly.

67. Theories Are Practical. — A boy who has learned to imagine what happens in the tube of his radio set is more likely to hook up his batteries properly than a boy who can see nothing more than a glowing filament within the bulb. Progressive business men are learning to say to themselves: "When in trouble, go to the theorist. He is the man who has been trained to see what ordinary eyes cannot see." Manufacturers often save themselves worry and make more money by realizing that a trained chemist is a person who has theories and an imagination which is more powerful than the microscope in getting at hidden causes of trouble.

68. Theories Are Needed to Explain Chemical Action. — Two substances unite and form a material which is different from either of the constituents. By analysis we can separate the new compound into the original substances. Our unaided senses are capable of showing us only the results of these changes, not the processes by which they were brought

about; but it has proved profitable to do some scientific guessing about such experiences. We use whatever facts we can discover, and base theories on these.

69. Matter is Indestructible. — The balance shows that after a chemical action, the total weight of substance is just what it was in the first place. In other words, chemical changes do not either increase or decrease quantity of matter. This generalization is known as the *Law of Conservation of Mass. There is no change in the total mass of matter taking part in any chemical change.* It is also sometimes put in this form: *Matter is indestructible.*

Conservation means neither increase nor decrease.

Mass means quantity of matter. For practical purposes, mass is measured by weighing.

70. Matter Is Made Up of Atoms. — Two other general statements that we can use in making theories are the law of definite proportions and the law of multiple proportions. From the first of these, it appears that the weights of elements in a chemical action are definitely regulated by something the eye cannot see, for they always stand in the same relation or comparison to each other, no matter how much of a compound is made, or what method of manufacture is chosen. From the second it appears that, using the chemist's scale of relative weights, oxygen goes into chemical action only in 16's; in sets of compounds made up of the same elements we find oxygen only in 16 parts, 32 parts, 48 parts, never in weights that are not multiples of 16. Similarly chlorine, if it makes two or more chlorides with the same metal, is found always in multiples of 35.5.

It is natural, therefore, to imagine that elements are made up of small particles. These particles must be very minute,

John Dalton (1766–1844) was an English schoolmaster, investigator, and mathematician. Dalton's work led up to the fundamental ideas of modern chemistry.

He studied rocks, dew, the weather, and various phenomena, notably those of gases, which he pictured as made up of small, elastic particles. While the idea of atoms was not original with Dalton, he experimented and collected data which showed that the facts could be explained by what we now call the atomic theory.

Dalton discovered the law of multiple proportions. He used this and the law of definite proportions in formulating the atomic theory. Dalton was the first to represent the atomic composition of compounds by symbols.

for no one has ever seen them even with the most powerful microscope. These unit particles are called *atoms*. They apparently do not divide in chemical action; for otherwise the law of multiple proportions would not be true.

The situation is something like that which might exist if a bookkeeper in a boarding school should try to tell without ever going near the kitchen whether eggs were served whole or scrambled. Suppose there are 80 pupils, and the bookkeeper notices that there is no regularity in the number of eggs used; that sometimes 69 eggs are cooked for breakfast, sometimes 87, sometimes 95. He would probably conclude that the boys were getting scrambled eggs or omelettes. But if he noticed that invariably 80 eggs were used for week days and 160 on Sundays, he would probably conclude that the eggs were served whole.

We cannot *see* whether elements combine with each other in scrambled fashion, or as fixed units. But we can see the total quantities that go into chemical action. We find fixed compositions and simple multiples to be the rule. Hence, like the bookkeeper in our example, who reasoned out that the eggs were served as units, we conclude that elements react with each other in the form of unbroken particles, which are never scrambled in chemical action.

The name *atoms* was given to the minute, indivisible particles by John Dalton, who discovered the law of multiple proportions and puzzled over it, seeking for an explanation, until he finally hit upon this idea of atoms. His theory has stood the test of nearly one hundred and twenty years, and it is now regarded as stating an actual truth. But if any one ever finds one clear case which does not agree with this idea of atoms, we shall have to alter the theory until it is in agreement with the new fact.

Growth has come in all the sciences by forming theories in the way we have just illustrated. The process goes on constantly; old theories are always giving way to new and better ones, or are being improved to fit newly discovered facts.

71. Characteristics of Atoms (Atomic Hypothesis). —

1. Atoms do not lose their identities in chemical action.
2. Atoms of the same elements are alike, but atoms of different elements are unlike.
3. Atoms of most elements have the power of uniting with atoms of other elements.

All atoms are exceedingly small. It is estimated that the diameter of an atom is less than a ten millionth of a centimeter.

An atom is the smallest part of an element taking part in a chemical change.

72. Atomic Weights. — It will be clear that the weight of an atom is one of its important characteristics. It is not necessary to determine the actual weight, and if we did, the number expressing it would involve a decimal so long that it would be very inconvenient to use. Instead, chemists require only *comparative weights* of atoms. The atom of oxygen is taken as standard because oxygen combines with most elements, and its value is placed at 16. This number is just large enough to make the number for the hydrogen atom, the lightest of all, slightly larger than 1. A table of the weights of the atoms of the elements is found on the inside of the back cover.

The atomic weight of an element is a number that expresses the weight of one of its atoms in comparison with the weight of an oxygen atom placed at 16.

73. Molecules. — When we have enough of an element to be seen, we do not necessarily have a simple collection of atoms, for the atoms of most elements have a tendency to unite into groups. Thus it is known that hydrogen gas is made up, not of separate atoms, but of groups of atoms, each of which contains two hydrogen atoms. A similar situation exists in the cases of oxygen, nitrogen, chlorine, and most other gaseous elements. All *compound* substances obviously must consist of some sort of combination of different atoms. When these are in the gaseous state it is known that the groups are comparatively simple. These simple groups of atoms are called *molecules*.

A molecule is the smallest part of a gas which has the chemical properties of the substance. Placed side by side, 250,000,000 molecules of oxygen would make a row one inch long.

In the case of helium and some other elements, the smallest particle consists of a single atom ; in these elements, atom and molecule are identical.

74. Symbols. — Everyone has seen water written as H_2O. This expression indicates our belief that water, when in the form of steam, is composed of molecules, and that each molecule consists of two atoms of hydrogen and one atom of oxygen. Similarly HCl stands for one molecule of hydrogen chloride, composed of one atom of hydrogen and one atom of chlorine.

A *symbol* consists of a letter or letters used to indicate one atom of an element. H, O, and Cl are symbols for hydrogen, oxygen, and chlorine, and each means one atom of the element. Usually the symbol for an atom of an element is the first letter in the name. When two elements begin with the same letter, in one case we must choose a second letter that

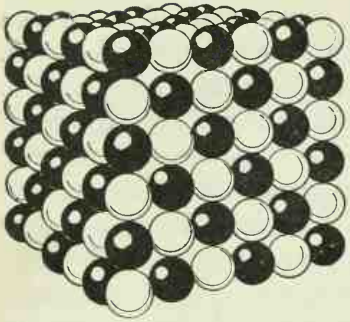


FIGURE 36.

In a crystal of potassium chloride the particles of potassium and chlorine alternate regularly. Hence the crystal is a cube.

is prominent in the name. A few of the elements were known in the days of the alchemists, when Latin names were the rule, and in such cases the symbol is derived from the old name. Examples: Hg, mercury; Pb, lead.

75. Formulas. — A *formula* is a collection of symbols together with subscript numbers which, in the case of gases, tell what atoms and how many of them are united to form the molecule of a substance. H_2, O_2, N_2, H_2O, HCl, are all formulas representing molecules of substances in the gaseous state.

76. A Theory Which Has Been Modified Lately. — Until a few years ago, it was believed that solids and liquids were like gases in being composed of separated molecules, each of which consisted of comparatively small numbers of atoms of elements present in the compound. But after Moseley began directing X-rays at crystals, it was discovered that atoms of solids and liquids were not grouped together into detached molecules as they are in gases. In a crystal of potassium chloride, for example, it was seen that the

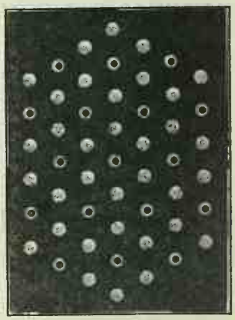


FIGURE 37.

The solid white dots represent hydrogen, the circles oxygen, as these elements are arranged in a crystal of ice. The pattern is hexagonal.

particles of potassium and chlorine were arranged in an interlacing, lattice-work pattern throughout the whole of the crystal (Fig. 36). In ice, the solid form of water, atoms of hydrogen and oxygen are arranged as shown in Figure 37. This explains the hexagonal form of ice crystals (Figs. 38, 39). It appears, then, that there are no separate molecules in solids, and a similar statement is probably true for liquids. Thus the theory of molecules was revised as a result of new observations.

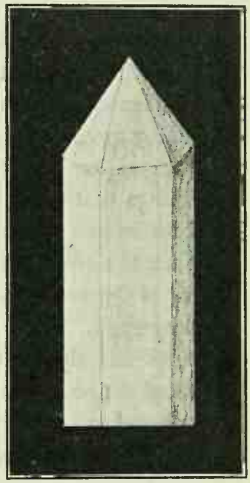
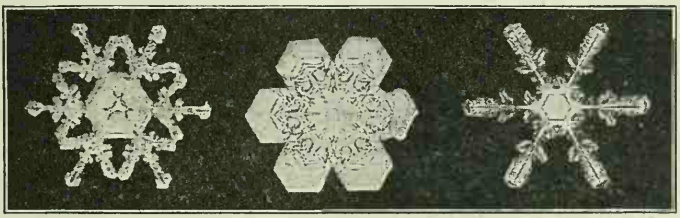


FIGURE 38.

How a large crystal of ice might look if we could obtain one in perfect form.

In potassium chloride, however, there is one atom of chlorine for every atom of potassium. Hence the formula KCl can be used to represent an important fact concerning the comparative numbers of the two kinds of atom. Similarly, while in a crystal of zinc sulphate there are no separated molecules of the substance, the formula $ZnSO_4$ indicates that for every



Courtesy of American Museum of Natural History.

FIGURE 39.

Actual photographs of snow flakes. While apparently so different, each shows the hexagonal tendency we should expect from the arrangement of the hydrogen and oxygen particles shown in Figure 37.

atom of zinc there is one atom of sulphur and four of oxygen.

SUMMARY

Hypotheses and theories are scientific guesses, based on all facts which have been discovered. They are not considered valuable unless they have proved reliable in making explanations or in making predictions concerning what is likely to happen.

Theories are useful because they aid the imagination to picture things that cannot be seen actually by the eyes.

Theories are necessary to understand chemical action because our eyes see only the results and not the way they are produced.

Law of Conservation of Mass. Matter can be neither created nor destroyed.

Atoms are the unit particles of elements which take part in chemical action. Since they are too small to be seen, we speak of our belief in them as the **atomic theory.**

The characteristics of atoms are: (1) Atoms are extremely small; (2) atoms retain their identity in chemical action; (3) atoms of the same element are alike; atoms of different elements are unlike; (4) atoms of most elements have the power of uniting with atoms of other elements.

Atomic Weights. Atoms of different elements have different weights. The standard is the weight of an oxygen atom, placed at 16. An atom of hydrogen is about one sixteenth as heavy as an oxygen atom; hence its atomic weight is approximately 1 (1.008). An atom of sulphur is twice as heavy as an oxygen atom; its atomic weight is 32. The atomic weight of an element is a number that expresses the weight of one of its atoms in comparison with the weight of an oxygen atom placed at 16.

A molecule is the smallest part of a gas which has the chemical properties of the substance. Usually a molecule consists of two or more atoms; they can be the same or different kinds of atoms.

A symbol consists of either one or two letters used to represent one atom of an element. A second letter is not used unless there are two elements whose names begin with the same letter.

A formula shows the kind and the comparative numbers of atoms in a substance. In case of gases the formula stands for one molecule of the substance.

EXERCISES

1. Why is imagination necessary in studying science?

2. What is the meaning of the word *theory?*

3. What danger is there in using the imagination? What in using hypotheses or theories?

4. What control is used by scientists in making use of theories?

5. Show how the atomic theory is of practical value.

6. What truth is there in the saying: "When in trouble go to the theorist"? What danger?

7. What does it mean to say that *matter is indestructible?*

8. What does the word *conservation* mean in the phrase *conservation of matter?*

9. What does the word *mass* mean as it is used in chemistry?

10. What are atoms? Give their characteristics.

11. What two laws state the general facts on which the idea of atoms is based?

12. How does the atomic theory explain or account for each of these laws?

13. Why was an extended study of the composition of substances necessary before the atomic theory could be reasonably accepted?

14. Mercury is put into a glass flask, which is then sealed, weighed, heated, and weighed again. Why is there no change in weight, although some of the mercury turns into a red powder?

15. Why is it that the attempt to make 2 grams of hydrogen combine with 17 grams of oxygen always leaves 1 gram of oxygen uncombined?

16. Dalton knew that one oxide of carbon contains $2\frac{2}{3}$ parts of oxygen to 1 part of carbon and that another oxide is composed of $1\frac{1}{3}$ parts of oxygen to 1 part of carbon. What law do these facts illustrate? Explain the facts according to the atomic theory.

17. Sulphur dioxide contains 50% of sulphur and 50% of oxygen. Sulphur trioxide contains 40% sulphur and 60% oxygen. Show how these facts can be used to illustrate the law of multiple proportions.

18. Dalton showed that for one part by weight of hydrogen, olefiant gas contains twice as many parts by weight of carbon as marsh gas does. Explain these facts according to the atomic hypothesis.

19. What is a molecule?

20. Is there any case in which a molecule consists of one atom?

21. What is a symbol? Is it an abbreviation for the name of an element or does it mean more than the name?

22. What is a formula? In what cases does it indicate the actual number of atoms in a molecule? In what cases does it indicate only the comparative number of different atoms?

23. Why do chemists use comparative weights of the atoms rather than actual weights?

24. What is the standard for atomic weights? Why is this element and this number chosen?

25. State the composition by weight of water and hydrogen peroxide. Give two laws illustrated by the compositions of these two compounds.

CHAPTER VI

THE USES OF SYMBOLS AND FORMULAS

77. Symbols and Formulas Indicate Weights. — The formula H_2 is more than an abbreviation for hydrogen. It indicates a definite weight of hydrogen. Since one hydrogen atom weighs 1 (approximately) in the scale based on oxygen taken as 16, the formula H_2 means two parts by weight of hydrogen. The formula H_2SO_4 indicates that one molecule of sulphuric acid is composed of 2 parts by weight of hydrogen, 32 parts of sulphur, and $4 \times 16 = 64$ parts of oxygen, and a total weight of 98 parts of sulphuric acid. This total is called the *molecular weight* of the compound. In the light of recent developments the term might better be *formula weight.* From these figures we can easily calculate the percentage composition of the substance (§ 226).

A more important use for formulas is found in writing chemical equations. For example, the word equation

sulphuric acid + zinc ⟶ zinc sulphate + hydrogen

hydrogen
sulphur
oxygen

zinc
sulphur
oxygen

may be written more simply, with the added advantage of expressing weight relations, by using formulas:

$$H_2SO_4 + Zn \longrightarrow ZnSO_4 + H_2$$

$2 + 32 + 64 \quad 65 \qquad 65 + 32 + 64 \quad 2$

$98 \qquad 161$

$98 + 65 = 163 \qquad 161 + 2 = 163$

The numbers written immediately under the formulas are the atomic weights of the elements in the compound multiplied, in each case, by the number of atoms present.

78. What an Equation Stands For. — Every chemical equation expresses several important things. Among them are:

(*a*) The law of conservation of mass. In the above example the sum of the reacting weights is the same on both sides of the arrow.

(*b*) The law of definite proportions. Each formula expresses the fact that the compound it represents has a constant, invariable composition.

(*c*) The equation indicates the weights of reacting material and the weights of products which may be expected. This fact is very useful to chemists in calculating the amounts of materials needed for reactions, and to manufacturers in estimating quantities they will have to buy and sell.

79. How Equations Are Written. — We must first know three things: (*a*) the names of the substances entering into the reaction; (*b*) the names of the new substances which are formed; and (*c*) the chemical formulas corresponding to each of these names. It is not always necessary to memorize each of these formulas separately, for each element has definite combining tendencies which enable us to *predict* formulas with a fair degree of certainty, and this knowledge can be used as an aid to the student's memory. These rules will be presented in Chapter XI under the topic of Valence.

Suppose, for example, that we wish to write the equation for the chemical action resulting when potassium chlorate is heated. We must know the experimental facts that oxygen is given off as a gas, and that potassium chloride remains in

Johann Jacob Berzelius (1779–1848) was a Professor of Chemistry in Stockholm. Although hampered by lack of means, he impressed himself and his ideas on the scientific world and became the leading figure in it.

Berzelius was an analytical genius; he repeated the work and extended the laws of Dalton to organic substances. He undertook the determination of atomic weights, taking the weight of oxygen as 100. His accuracy enabled him to discover several elements. He tried to explain molecular structure and developed the electrochemical theory, which, though later modified by himself and others, has proved of great service. He introduced the use of initial letters as symbols of atoms.

the test tube. We must know also that the formula of potassium chlorate is $KClO_3$, that the formula of oxygen is O_2, and that the formula of potassium chloride is KCl. We are then justified in writing

$$KClO_3 \longrightarrow O_2 + KCl$$

But if we examine this expression we see that it does not tell the truth; that we have only *two* atoms of oxygen on the right while there are *three* on the left, and that our equation so far fails to express the law of conservation of mass. To correct this inaccuracy, we must now *balance* the equation.

80. Balancing an Equation. — This is done by putting in numbers, if necessary, before each of the chemical formulas, so that finally there will be the same number of atoms of any element on the two sides of the equation. These inserted numbers tell the minimum number of formula weights that could be concerned in the action. The oxygen molecule always contains two atoms. It is clear, therefore, that if potassium chlorate gives off all its oxygen, one formula weight would yield *three*, and not two, atoms of oxygen; but two formula weights of potassium chlorate can yield three molecules of oxygen, for the total number of oxygen atoms in each case is six. Thus we are now justified in writing:

$$2\ KClO_3 \longrightarrow 3\ O_2 + KCl$$

But there is still further error; there are two atoms of potassium and two atoms of chlorine on the left, while there is only one of each of these elements on the right. This discrepancy is easily corrected by writing a 2 before the formula of potassium chloride:

$$2\ KClO_3 \longrightarrow 3\ O_2 + 2\ KCl$$

When this is done we have a correct, *balanced,* chemical equation.

Numbers needed for balancing are usually found by simple mental calculation. The most common difficulty exists when a formula on one side has an odd number of atoms of a given element, while a formula on the other side has an even number of atoms of the same element, as in the example just given. The difficulty is met by thinking of a number which can be divided evenly by both the odd and the even digit. For example, in the above case, we thought of six as a number which can be divided by both two and three. Balancing is always done by putting in the right number before the formula ; *never by altering subscript numbers.*

When we know all the substances taking part in, and formed by, a chemical reaction, we can always write a complete balanced equation, which indicates correctly the weights concerned in the reaction. This fact is strong evidence in support of the hypothesis of atoms, the law of definite proportions, and the law of the conservation of mass. The possibility of indicating in a simple way so many of the facts about chemical action has been of incalculable importance in the development of the science of chemistry. Every student of the science must, therefore, learn the device of the chemical equation early in his course.

81. Solving Weight Problems in Chemistry. — Suppose we desired to make 20 grams of oxygen without wasting material. We can proceed as follows:

Write the chemical equation for the action —

$$2\ KClO_3 \longrightarrow 3\ O_2 + 2\ KCl$$

State the problem simply, and clarify the purpose by writing 20 grams above the formula of the substance we desire to

get, and an x above the formula of the substance which must be weighed in advance.

$$\begin{array}{ccc} x \text{ grams} & & 20 \text{ grams} \\ 2\,KClO_3 & \longrightarrow & 3\,O_2 + 2\,KCl \end{array}$$

Then below the formulas write the formula weights which concern the problem, calculating them from the atomic weights (K = 39, Cl = 35.5, O = 16).

Actual weights	x grams		20 grams
	$2\,KClO_3$	$\longrightarrow$	$3\,O_2 + 2\,KCl$
Atomic weights	$39 + 35.5 + 3 \times 16$		2×16
Formula weights	122.5		32
Equation weights	245		96

Note that the number written before a formula weight is used as a multiplier to get the *equation weight.* The numbers for potassium chloride are not written because they do not enter into this particular problem.

Our problem may now be stated thus: How many grams of potassium chlorate are needed to produce 20 grams of oxygen, knowing from the equation that 245 grams of potassium chlorate *always* produce 96 grams of oxygen. It is wise at this point to make a "guess" answer. We see easily that 245 is about two and one half times 96. Hence common sense tells us that our answer will be about two and a half times as great as the 20 grams of oxygen we desire to get. Therefore our result will be in the neighborhood of 50 grams of potassium chlorate. A little forethought of this kind will save writing as an answer some absurd number resulting from carelessness in arithmetic.

To get the exact result use a device learned in arithmetic known as the proportion:

$$245 : 96 :: x \text{ grams} : 20 \text{ grams}$$

The student will remember that, if the proportion is correctly stated, the product of the two end numbers is equal to the product of the two middle numbers.

$$96\,x = 245 \times 20 \text{ grams}$$
$$96\,x = 4900 \text{ grams}$$
$$x = 51.0 \text{ grams} \quad \textit{Answer.}$$

This answer agrees well with our " guess " answer.

82. Summary of Problem Steps. — It results in great economy of time and saves errors to learn to do such problems in a systematic manner. Summarizing, the student should work carefully, step by step, as follows:

(1) Make sure that he knows all the substances needed in the action and all substances formed.

(2) Make sure that he knows the formulas of all these substances.

(3) Make sure that the equation is *balanced;* never alter the subscript numbers in the formulas while balancing.

(4) Write x above the formula of the substance whose weight is being calculated, and the known weight in gram ounces or pounds above the formula of the substance whose actual weight is given.

(5) Write under the formula of each substance named in the problem (and under these only) its equation weight.

(6) Make a " guess " answer.

(7) Write a proportion consisting of two ratios. The first ratio contains the equation weights that were written below the equation; the second ratio, the numbers above the equation. The numbers in both ratios should stand in the same order in which they were written in connection with the equation.

(8) Solve the proportion.

(9) Check the computed answer against the "guess" answer.

83. Special Points about Problems. — The x can be on either side of the arrow. In other words, we can calculate (1) the weight of any product if we know the weight of any material used; or (2) the weight of any material needed to give a desired weight of any product.

The x and the known weight may also be on the same side of the arrow. In other words, if we know the weight of any material used, we can calculate the weight of any other material in the equation. *Example:*

What weight of hydrogen will be needed to react with 100 grams of iron oxide in the action represented by the equation iron oxide + hydrogen ⟶ iron + water?

Proceeding according to the numbered steps:

(1) Iron oxide and hydrogen are needed for the reaction, and iron and steam result from it.

(2) The formula of iron oxide (in this case) is Fe_3O_4, of hydrogen is H_2, of iron is Fe, of steam is H_2O.

(3) $Fe_3O_4 + H_2 \longrightarrow Fe + H_2O$.

But the equation is not balanced; there are 4 atoms of oxygen on the left; hence we must write 4 in front of H_2O; there are 3 atoms of iron on the left and only 1 on the right; hence we must write 3 in front of the Fe; there are (now) 2 atoms of hydrogen on the left and 8 on the right; hence we must write 4 in front of the H_2. We now write the balanced equation and include steps (4) and (5):

(4) Actual weights	100 grams		x grams			
(3) Balancing	Fe_3O_4	+	$4\,H_2$	⟶	$3\,Fe + 4\,H_2O$	
(5) Atomic weights	$(3 \times 56) + (4 \times 16)$		2×1			
Formula weights	$168 + 64$		2			
Equation weights	232		8			

(6) 232 is about 30 times 8; hence the answer will be about one thirtieth of 100, which is somewhere between 3 or 4 grams.

(7) 232 : 8 : : 100 grams : x grams

(8) $232\,x = 800$ grams

$x = 3.45$ grams *Answer*

(9) This answer agrees well with our "guess" answer.

The solution of the problem may be arranged more simply as follows:

$$\begin{array}{rcl} 100 \text{ grams} & & x \text{ grams} \\ Fe_3O_4 & + & 4\,H_2 \longrightarrow 3\,Fe + 4\,H_2O \\ Fe_3 = 168 & & H_2 = 2 \\ O_4 = \underline{\ 64} & & \\ Fe_3O_4 = 232 & & 4\,H_2 = 8 \end{array}$$

232 : 8 : : 100 grams : x grams

$x = 3.45$ grams *Answer*

SUMMARY

A formula (or molecular) **weight** is the sum of the weights of the atoms represented by the formula. From formulas we can determine percentage composition of substances, because each symbol in the formula stands for an atomic weight of the element it represents.

Chemical equations are expressions which use formulas to show what substances are put together to produce a given chemical action, and what substances are formed as products. The two sides of an equation are separated by an $\longrightarrow$. Because of the weight meanings of formulas, chemical equations tell us how much of each of the substances should be used, and how much of the products may be expected.

To write a chemical equation we must

(1) know what substances are needed and what substances result, as proved by experiment;

(2) know the chemical formulas of all the above substances;

(3) calculate the number of formula weights needed to make the equation balance.

To calculate weights of substances concerned in chemical action, proceed according to steps (4) to (9), pages 72 and 73.

EXERCISES

1. How is a formula weight calculated?

2. What is a chemical equation? Why is it better to use formulas rather than ordinary names in writing such an equation?

3. Why is a knowledge of chemical equations and of formula weights useful in manufacturing chemical compounds?

4. Why cannot the products of a chemical factory weigh more than the materials used to make them?

5. Write the name of each substance under its formula and balance the equation in each case:

$$Cu + O_2 \longrightarrow CuO$$
$$Pb + O_2 \longrightarrow PbO$$
$$Sn + O_2 \longrightarrow SnO_2$$
$$Hg + O_2 \longrightarrow HgO$$
$$HgO \longrightarrow Hg + O_2$$
$$KClO_3 \longrightarrow O_2 + KCl$$
$$C + O_2 \longrightarrow CO_2$$
$$O_2 \longrightarrow \underset{\text{ozone}}{O_3}$$
$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$
$$H_2O + Fe \longrightarrow Fe_3O_4 + H_2$$
$$H_2 + O_2 \longrightarrow H_2O$$
$$H_2O \longrightarrow H_2 + O_2$$
$$Zn + H_2SO_4 \longrightarrow H_2 + ZnSO_4$$
$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

6. The above equations all express chemical actions that you have either performed in the laboratory, or that have been

referred to in previous chapters. Tell briefly what was taught by each of these experiments.

7. How many pounds of copper oxide would be obtained by oxidizing completely 127 pounds of copper?

8. How many grams of mercuric oxide would be needed to produce 64 grams of oxygen?

9. How many ounces of zinc chloride would result from the complete reaction of hydrochloric acid on 32.5 ounces of zinc?

10. How many grams of zinc would be needed to produce 4 grams of hydrogen by reaction with hydrochloric or sulphuric acid?

11. What weight of sulphuric acid is needed for reaction with 50 grams of barium peroxide? What weight of barium sulphate will result from this reaction? What weight of hydrogen peroxide?

12. If a student should put 65 grams of zinc and 107 grams of sulphuric acid into his hydrogen generator, which of the two substances would be partly wasted? How much of it?

13. How many pounds of hydrogen might we expect to get by the electrolysis of a ton of water?

14. How much will the product weigh when 5 grams of lead have been completely converted into lead oxide (PbO)?

15. If copper costs 14 cents a pound and the labor of converting it into copper oxide amounts to 2 cents more, at what price could copper oxide be sold to yield a profit of 10 per cent?

16. How many pounds of carbon dioxide should be obtained from a ton of coke that contained 90 per cent uncombined carbon?

17. How much mercury can be obtained from a kilogram of mercuric oxide? (1 Kg = 1000 g.)

18. How much potassium chloride would be obtained in using potassium chlorate to prepare 20 grams of oxygen?

CHAPTER VII

CHLORINE

84. Introduction. — Chlorine displays in a marked degree those properties which are characteristic of the non-metals. The most abundant compound of chlorine found in nature is sodium chloride, common salt. Sodium chloride is a very stable compound; heat does not decompose it except at an extremely high temperature. From sodium chloride chlorine can be obtained in several ways.

85. Preparation by Electrolysis. — An electric current can be passed through a solution of common salt, using apparatus similar to that used in the electrolysis of water. The electrodes in this case, however, should be of carbon, since platinum slowly combines with the chlorine that is evolved. The apparatus is filled with a concentrated solution of salt. When the current passes, chlorine is evolved as a gas at the anode and hydrogen at the cathode. Sodium is probably first liberated at the cathode; but since this element reacts rapidly with water, it is impossible for it to accumulate. Hydrogen is set free as a result of the action of sodium with water.

$$\underset{\text{sodium chloride}}{2\,NaCl} \longrightarrow \underset{\text{sodium}}{2\,Na} + \underset{\text{chlorine}}{Cl_2}$$

$$\underset{\text{sodium}}{2\,Na} + \underset{\text{water}}{2\,H_2O} \longrightarrow \underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{hydrogen}}{H_2}$$

As the final products, we have the two gases, hydrogen and chlorine, together with sodium hydroxide which is dissolved in the water.

86. Laboratory Preparation by Oxidation of Hydrochloric Acid. — Hydrochloric acid is a solution of a compound of hydrogen and chlorine. If we oxidize hydrochloric acid, the hydrogen will combine with the oxygen to form water, and free chlorine will be obtained.

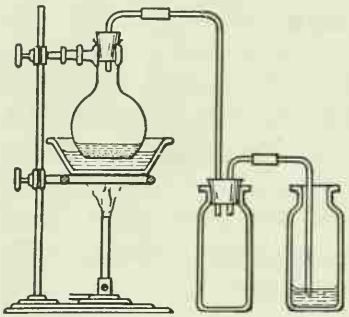


FIGURE 40.

Manganese dioxide and hydrochloric acid when gently warmed in a pan of water yield chlorine. This fills the first bottle and then passes on to be dissolved in the water contained in the second.

Often manganese dioxide is the oxidizing agent employed. Concentrated hydrochloric acid solution is mixed with manganese dioxide; when the mixture is warmed, chlorine is evolved (Fig. 40). The hydrogen of the acid combines with the oxygen of the dioxide, forming water. The manganese combines with half the chlorine of the acid, forming manganese chloride, which dissolves in the water; the remaining portion of the chlorine is evolved as a gas:

$$4\,HCl + MnO_2 \longrightarrow 2\,H_2O + MnCl_2 + Cl_2$$

hydrochloric acid — manganese dioxide — water — manganese chloride — chlorine

Since dry chlorine is desirable for many experiments, the chlorine is not usually collected over water, because water dissolves chlorine at ordinary temperatures. It is commonly collected by displacement of air, or over salt water, in which it is scarcely soluble. Its heaviness and color render its collection by displacement of air a simple matter.

A mixture of salt, sulphuric acid, and manganese dioxide is often used in preparing chlorine. The salt and sulphuric

acid react and form hydrochloric acid, which is then oxidized by the manganese dioxide, liberating the chlorine.

87. Physical Properties. — Chlorine is a greenish yellow gas, nearly two and one half times as dense as air; water will dissolve twice its volume of chlorine, and the solution is commonly known as *chlorine water.*

Chlorine has an intensely disagreeable odor, and attacks the membrane of the nasal passages and lungs, producing effects something like those of a bad cold. It is very poisonous; a full breath of the pure gas would probably cause death. Inhaling ammonia or alcohol will counteract some of the effects. Chlorine should be prepared and handled with caution to prevent any possibility of inhaling it. Chlorine was the first of the poison gases used in the Great War. It is easily liquefied, and the liquid chlorine is transported in steel cylinders.

Chemical Properties

88. Action with Metals. — Chlorine is a very active element. It combines directly with many other elements, especially metals, forming chlorides. When freshly powdered antimony is sprinkled into a jar of chlorine, brilliant sparks are seen and a white cloud of antimony chloride is produced. Zinc, copper, iron, and most other metals, especially when heated, also unite readily with chlorine, and chlorides of these elements are formed:

$$\underset{\text{antimony}}{2\,Sb} + \underset{\text{chlorine}}{3\,Cl_2} \longrightarrow \underset{\substack{\text{antimony}\\\text{chloride}}}{2\,SbCl_3}$$

$$\underset{\text{zinc}}{Zn} + \underset{\text{chlorine}}{Cl_2} \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2}$$

These are true cases of combustion, since heat and light appear. So we may say chlorine supports combustion, and thus resembles oxygen.

When molten sodium comes in contact with chlorine, it blazes with a dazzling light, sodium chloride (common salt) being formed. To one who for the first time observes the change, it seems almost incredible that a gas possessing the disagreeable and poisonous properties of chlorine will combine with a metal (sodium) that has sufficient energy to decompose water, to produce a harmless household necessity like common salt.

89. Action with Free Hydrogen. — If a jet of hydrogen is ignited in the air and lowered into a jar of chlorine, a pale, nearly white flame will be produced; the color of the chlorine will disappear, and in the jar we shall find a colorless gas, hydrogen chloride, which fumes strongly in moist air.

$$\underset{\text{hydrogen}}{H_2} + \underset{\text{chlorine}}{Cl_2} \longrightarrow \underset{\text{hydrogen chloride}}{2\,HCl}$$

Much heat is given off in the union of chlorine with hydrogen — another similarity between the behavior of chlorine and oxygen. Chlorine and hydrogen will not combine in the dark; in diffused daylight they combine slowly, and explode when exposed to direct sunlight or other bright light.

90. Action with Combined Hydrogen. — The great tendency of chlorine to combine with hydrogen is shown by the fact that it will abstract hydrogen from many compounds. Turpentine is a compound of carbon and hydrogen. If a piece of paper is moistened with warm turpentine and thrown into a jar of chlorine, a violent action occurs, often with the production of a flame, and a heavy deposit of soot

(carbon) forms on the sides of the bottle. An action similar to that with the turpentine is seen in the burning of a wax taper in chlorine. Paraffin wax, like turpentine, contains carbon combined with hydrogen, and only the latter unites with the chlorine. If the breath is blown into the bottle, the moisture will cause the hydrogen chloride there to fume.

91. Action with Water. — Although water is a very stable substance, under certain circumstances chlorine will react with it, combining with the hydrogen to form hydrogen chloride and setting the oxygen free. If a tube is filled with a solution of chlorine in water and is allowed to stand in the sunlight, oxygen is slowly formed and collects at the top of the tube (Fig. 41):

$$\underset{\text{water}}{2\,H_2O} + \underset{\text{chlorine}}{2\,Cl_2} \longrightarrow \underset{\text{oxygen}}{O_2} + \underset{\text{hydrochloric acid}}{4\,HCl}$$

The hydrogen chloride formed is dissolved by the water. Chemical actions brought about by the action of light are not uncommon; an important example is the formation of starch in the green leaves of plants under the influence of sunlight. Photographic processes also depend on the effect of light in promoting chemical action.

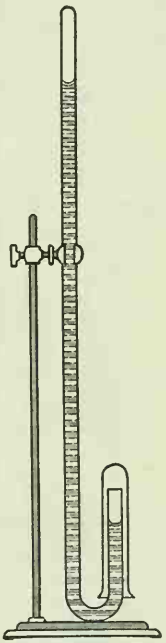
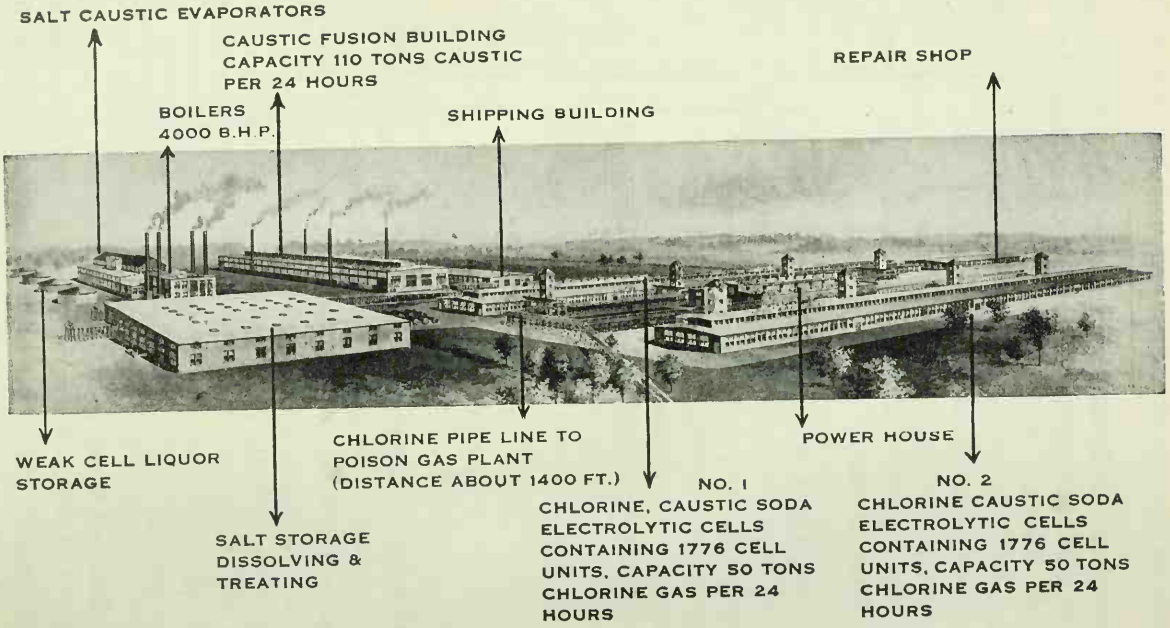


FIGURE 41.

The gas in the upper part of the tube is oxygen that has resulted from the reaction of chlorine with water under the influence of strong sunlight.

92. Chlorine Water is a Good Oxidizing Agent. — Chlorine is able to decompose water in the absence of light, provided there is present an oxidizable substance.



UNITED STATES OF AMERICA CHLORINE AND CAUSTIC SODA PLANT

CAPACITY 110 TONS OF CAUSTIC SODA AND 100 TONS OF CHLORINE PER 24 HOURS

For this reason chlorine water is a good *oxidizing agent;* the chlorine combines with the hydrogen of the water, and the oxygen set free combines with the reducing material present. The use of chlorine in bleaching cotton cloth depends on this fact (§ 94).

Manufacture and Uses

93. Manufacture. — On a commercial scale, the electrolysis of brine has given rise to many obstacles. Among

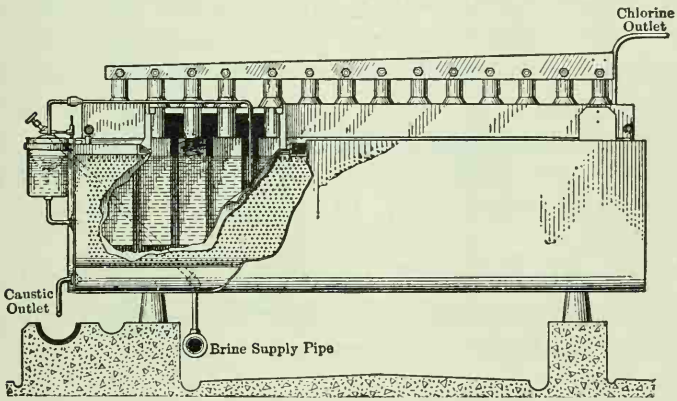


FIGURE 42.

The Nelson cell for manufacturing chlorine and caustic soda.

the many cells devised for the production of large quantities of pure chlorine, the Nelson cell has attracted great attention, owing to the fact that during the Great War, 3500 of these cells, capable of making 100 tons of chlorine each day, were installed at the Edgewood Arsenal, Maryland.

The cell consists of a rectangular steel box (Fig. 42), in which is placed a perforated, U-shaped trough of sheet steel, which acts as the cathode. This runs the length of the

cell, and is closed at the ends by cement blocks. The pure brine is automatically fed into this central chamber. The anodes are suspended in this trough. They are bars of graphite specially treated so that they will last a long time. An asbestos diaphragm lines the inside of the perforated cathode and is supported by it. As we have already explained (§ 85), the chlorine is set free at the graphite anodes, and sodium hydroxide is formed on the steel cathode. The brine passes through the diaphragm to the space outside the cathode, carrying with it sodium hydroxide formed during the action. The caustic soda is separated from the salt by evaporating and crystallizing the liquor from the cathode compartment; the chlorine is led off the top of the anode chamber. The purpose of the diaphragm is to prevent the mixing of the chlorine and the sodium hydroxide solution, because they would react. In operation, the cell is kept hot by steam.

A standard Nelson cell under normal operating conditions produces 68 pounds of sodium hydroxide and 60 pounds of chlorine (99% pure) every twenty-four hours.

94. Bleaching. — The chief commercial use of chlorine is as a bleaching agent, especially for cotton goods. Cotton fiber is not naturally *white*. When unbleached cotton goods are placed in a jar of chlorine, no action takes place if neither the cloth nor the chlorine is moist; but if moisture is present, the color is destroyed (Fig. 43). In this case, the chlorine unites with the water, forming hydrochloric acid and an unstable compound known as hypochlorous acid (HClO):

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{hydrochloric acid}}{HCl} + \underset{\text{hypochlorous acid}}{HClO}$$

Hypochlorous acid easily gives up its oxygen, particularly in the presence of easily oxidizable materials, such as some dyes and the coloring matter of many fibers:

$$\underset{\text{hypochlorous acid}}{HClO} + \text{oxidizable matter} \longrightarrow \underset{\text{hydrochloric acid}}{HCl} + \text{oxidized matter}$$

Some dyes are not bleached by chlorine. Some coloring matters are bleached because the chlorine combines with

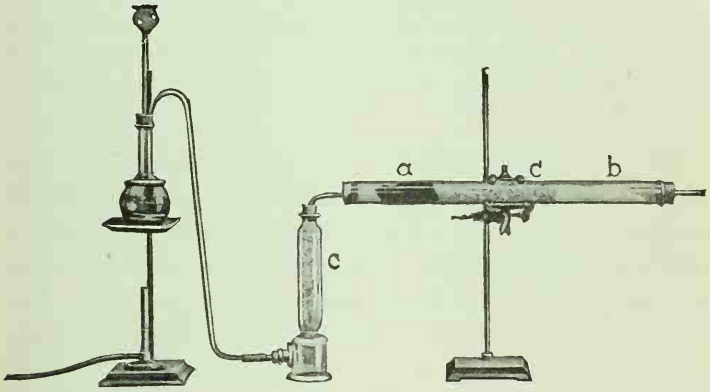


FIGURE 43.

a is dry, colored cloth; *b* is a bit of the same cloth that has been moistened; *c*, *c* are lumps of calcium chloride that keep moisture from the dry cloth.

the hydrogen of the dye. Chlorine cannot be used to bleach silk and wool, as it destroys the fibers themselves.

In bleaching, chlorine gas is not so generally used as is bleaching powder, a compound obtained by absorbing chlorine in slaked lime. When an acid is added to bleaching powder, chlorine is liberated. Thus in the commercial bleaching of cotton, it is soaked in a mixture of bleaching powder and water, and then run into dilute acid to liberate the chlorine. This in turn combines with the water, giving hypochlorous acid which does the actual bleaching. The

excess of chlorine is removed from the cotton by the use of some chemical that reacts with chlorine. Finally the cotton is thoroughly washed to remove all chemicals (Fig. 44).

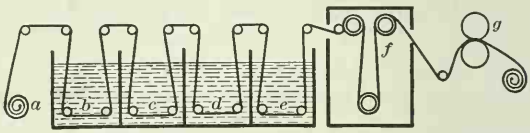


FIGURE 44. — HOW COTTON CLOTH IS BLEACHED IN FACTORIES.

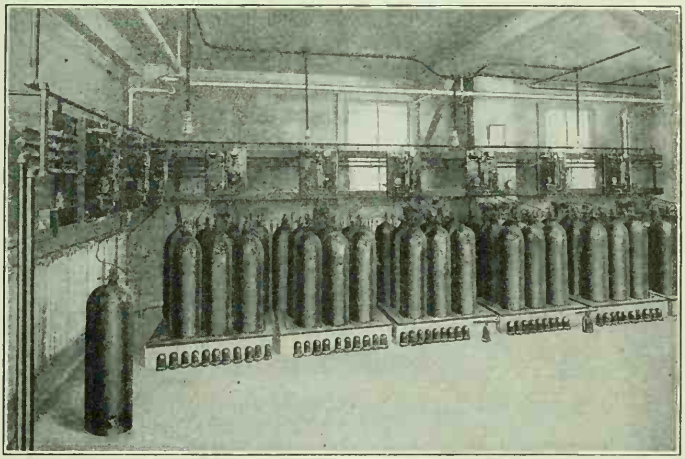
The cloth *a* rolls through a vat *b* containing bleaching powder solution, then through *c*, which contains dilute acid. *d* is a solution of sodium sulphite that absorbs the excess of chlorine. In *e* the cloth is washed; *f* and *g* are drying and ironing devices.

95. Disinfecting. — Chlorine is a good disinfectant, because it reacts with protein material and kills microscopic organisms, including disease germs. Bleaching powder (chloride of lime) affords a convenient means of transporting and using chlorine for this purpose; on standing exposed to air, chlorine is slowly given off. The carbon dioxide of the air unites with water to form a weak acid, carbonic acid, which reacts with bleaching powder, liberating chlorine. This gas can also be rapidly liberated by the addition of any common acid to the bleaching powder. Bleaching powder is one of the cheapest and most widely used disinfectants.

The sodium compound analogous to bleaching powder is sodium hypochlorite. It is also produced by the electrolysis of brine, and is used for the same purposes as chlorine and bleaching powder. Javelle water is a solution of sodium hypochlorite, made by the reaction between bleaching powder and sodium carbonate. It is a very convenient household bleach for removing fruit and other stains. Dakin's and Carrel's solutions are similar to Javelle water. Zonite is one of the trade preparations of such solutions. They

are carefully controlled as to alkalinity and chlorine content, and were much used in the war for cleansing deep wounds.

Both chlorine itself and hypochlorites are extensively used in the purification of drinking water. Liquid chlorine is commercially obtainable in steel cylinders. It is frequently used in water purification, as shown in Figure 45, and for many other industrial purposes.



Courtesy of the Wallace and Tiernan Co.

FIGURE 45.

The largest chlorinating plant in the world. 400,000,000 gallons of water a day flowing to New York City are treated with chlorine in this plant at Dunwoodie, New York.

96. Other Uses. — Important uses of chlorine are in the making of carbon tetrachloride, important as a solvent and as a material for fire extinguishers; chloroform, an important anæsthetic; sulphur chloride, used in vulcanizing rubber. Chlorine is also used in extracting metals from their ores, and in recovering tin from old tin cans and scrap tin plate. It is of great service to mankind.

SUMMARY

Chlorine occurs in nature combined with metals, its most important compound being salt.

Chlorine is prepared: (1) by the electrolysis of brine; (2) by the oxidation of hydrochloric acid; (3) by the action of salt with a mixture of manganese dioxide and sulphuric acid. The first is the common commercial method.

Properties. — Atomic weight, 35.5. Density, 3.2 grams per liter. One volume of water at ordinary temperature dissolves about two volumes of chlorine.

Chlorine is a greenish yellow, poisonous gas, characterized by a pungent odor and by its chemical activity. It reacts with metals to form chlorides, and with hydrogen and many hydrogen compounds to form hydrogen chloride. Its reaction with water, yielding hypochlorous acid which furnishes oxygen, is used in bleaching and in disinfecting.

The principal **uses** of chlorine are for bleaching, disinfecting, extraction of metals from ores, and the purification of water.

EXERCISES

1. In the electrolysis of a water solution of sodium chloride: (*a*) Why is sodium not obtained as one of the final products? (*b*) Why are carbon electrodes used? (*c*) What are the three final products and how are they separately obtained? (*d*) Write the chemical equations for the electrolysis.

2. Name two chemicals used in the laboratory preparation of chlorine. State why each is used. Write the chemical equation for the preparation.

3. In the mixture of salt, sulphuric acid, and manganese dioxide, used in the preparation of chlorine, what is the purpose of each?

4. Why can chlorine be readily collected by (*a*) the displacement of air; (*b*) over salt water?

5. In what two ways is chlorine transported? Why?

6. Describe a case of combustion in which oxygen is not involved.

7. Compare chlorine and oxygen with respect to their chemical activity with hydrogen and with metals.

8. What happens to a mixture of chlorine and hydrogen: (*a*) in the dark; (*b*) in the ordinary light of a room; (*c*) in direct sunlight?

9. Account for the black smoke produced when turpentine burns in chlorine.

10. Make a labeled drawing of an apparatus that will enable you to get oxygen from a water solution of chlorine. Write the equation for the reaction.

11. What is *chlorine water?* Under what conditions will it readily act as an oxidizing agent?

12. When chlorine water is to be used for testing purposes in the laboratory, why should it always be freshly prepared?

13. Give the purpose of (*a*) the U-shaped trough, (*b*) the bars of graphite, (*c*) the diaphragm in the Nelson cell. What two important commercial products are produced by this cell?

14. Explain, with the aid of equations, the action of chlorine on colored cloth when wet.

15. Name two fibers that should not be bleached by chlorine. Why? What substance already studied is used to bleach wool?

16. How is bleaching powder made? What is the action of acids upon it?

17. Why is chlorine liberated from bleaching powder by the reaction with carbon dioxide of the air? What use of bleaching powder depends upon this last action?

18. What is Javelle water? Mention two of its household uses.

19. Why are water supplies treated with chlorine? Name two sources of chlorine for this purpose.

20. Give two cases in which light produces or hastens chemical action.

21. Make a labeled diagram of a commercial process for bleaching cloth. Briefly state the steps in the process.

22. If you accidentally inhaled some chlorine in the laboratory, what means would you employ to counteract its effects?

23. When a piece of iron wire is heated red hot and plunged into a jar of chlorine, it burns, forming $FeCl_3$. Write the equation for the action.

24. Calculate the weight of ferric chloride which would be formed if 5 grams of iron were consumed in the reaction required in Exercise 23.

CHAPTER VIII

HYDROCHLORIC ACID

97. Preparation. — Hydrochloric acid is the water solution of hydrogen chloride, which is one of the most important compounds of chlorine. It may be made by the direct union of hydrogen and chlorine, but the combination is so violent and so hard to control that its preparation in this way is not suitable for the laboratory. It is more conveniently prepared by taking a chloride, *e.g.* sodium chloride, and adding concentrated sulphuric acid (Fig. 46). The action begins immediately, and the gaseous hydrogen chloride is evolved so easily that little heating is necessary. Too violent action may be avoided by the successive additions of small quantities of the sulphuric acid to the chloride, and by using a pan of hot water to heat the mixture. The action may be represented thus:

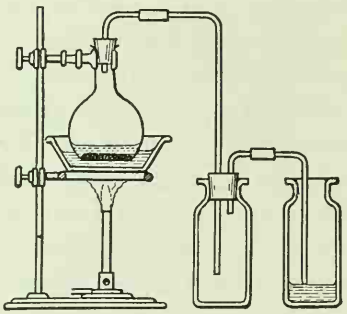


FIGURE 46.

The gentle heating of salt and concentrated sulphuric acid over a pan of hot water produces hydrogen chloride, which is collected as a gas in the first bottle and as a solution, hydrochloric acid, in the second bottle.

$$\underset{\text{sodium chloride}}{NaCl} + \underset{\text{sulphuric acid}}{H_2SO_4} \longrightarrow \underset{\text{sodium hydrogen sulphate}}{NaHSO_4} + \underset{\text{hydrogen chloride}}{HCl}$$

The chlorine of the salt combines with half of the hydrogen from the sulphuric acid, and the sodium with the remaining part of the sulphuric acid.

The hydrogen chloride gas may be collected by the downward displacement of the air, or, better, over mercury, since this metal is not attacked by the gas. More frequently, however, the gas is dissolved in water, forming hydrochloric acid, and this acid solution is used.

98. General Method for Preparing Acids. — The preparation of hydrochloric acid illustrates a general method for preparing acids that do not have very high boiling points. Sulphuric acid is used because it boils (vaporizes) only at a comparatively high temperature (338° C.), while hydrochloric acid vaporizes at a much lower temperature. When the sulphuric acid comes in contact with a chloride, a reaction occurs and some hydrochloric acid is formed. The excess of sulphuric acid, the newly formed hydrogen chloride and its solution, hydrochloric acid, are then present in the mixture. The hydrochloric acid, however, is soon vaporized, since its boiling point is many degrees below that of sulphuric acid. The higher boiling sulphuric acid remains behind and gradually completes its reaction with the sodium chloride. Finally, all the hydrogen chloride is driven off and any excess of sulphuric acid remains mixed with the sodium hydrogen sulphate. Sulphuric acid is generally used in the preparation of other acids because of its high boiling point.

99. Physical Properties. — Hydrogen chloride is a colorless gas with a sharp, penetrating odor. It is heavier than air. Its solubility in water is most striking, between four and five hundred volumes of the gas dissolving in one volume of water at room temperature. This solution, commonly

known as hydrochloric acid or muriatic acid, contains about 38% by weight of the hydrogen chloride. The high solubility of the gas causes it to condense the moisture of the air. The minute particles of the resulting liquid appear as a white mist, or as fumes. This effect can be seen when a concentrated solution of hydrochloric acid is exposed to the air. The fuming is still more marked when the moist breath is

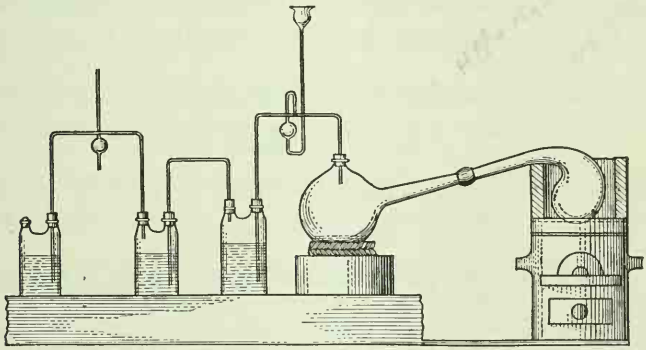


FIGURE 47.

An ancient apparatus for obtaining a concentrated solution of hydrogen chloride in water. The retort contains concentrated sulphuric acid and sodium chloride. Heat is supplied by burning charcoal. Fuel gas and bunsen burners were unknown things in those days.

blown across the mouth of a tube from which hydrogen chloride gas is issuing, and this fact is used as a means of recognizing the gas.

Hydrogen chloride can be liquefied and also solidified at low temperatures with increased pressure.

100. Chemical Properties. — Hydrogen chloride, when perfectly dry, does not show the chemical properties characteristic of the acids. These properties belong to the water solution. Hydrochloric acid, then, is the aqueous

solution of hydrogen chloride. The water solution has a sour taste, changes blue litmus to red, and reacts with many metals, setting free hydrogen and forming a chloride of the metal.

Four common metals with which hydrochloric acid does not react to any great extent are mercury, silver, copper, and lead. These metals are exceptional in their action with acids in general. Zinc and iron are typical of the metals with which hydrochloric acid does react readily. The equations are:

$$\underset{\text{zinc}}{Zn} + 2\,\underset{\text{hydrochloric acid}}{HCl} \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2}$$

$$\underset{\text{iron}}{Fe} + 2\,\underset{\text{hydrochloric acid}}{HCl} \longrightarrow \underset{\text{iron chloride}}{FeCl_2} + \underset{\text{hydrogen}}{H_2}$$

In these actions the metal replaces the hydrogen in the acid, forming a *chloride.*

101. Typical Properties of Acids. — The compounds commonly known as *acids* are characterized by certain properties.

The sour taste of acids is an interesting but not an important distinguishing property. Many fruits owe their sour taste to the presence of acids. Vinegar is hardly more than a dilute solution of acetic acid. The change in color of litmus and of other organic coloring matters is a convenient way of recognizing acids, but is not reliable in all cases.

Acids are substances which contain hydrogen that may be replaced by metals, and whose water solutions turn litmus red.

Substances, such as sugar, whose hydrogen cannot be replaced by metals, are not classed as acids. In general,

$$\text{metal} + \text{acid} \longrightarrow \text{salt of the metal} + \text{hydrogen}$$

When an acid reacts with a metal, hydrogen is generally evolved as a gas unless there is an oxidizing agent in the solution, in which case the hydrogen may be oxidized to water.

102. Salts. — A compound formed by the replacement of hydrogen in an acid by a metal is called a *salt*. The salt is usually found dissolved in the water that was used to dilute the acid. The portion of an acid molecule remaining after all replaceable hydrogen has been removed is called an *acid radical*.

A salt is a metal combined with an acid radical.

103. Chlorides. — Hydrochloric acid, like chlorine, reacts with many metals, forming chlorides.

metal + hydrochloric acid ⟶ metallic chloride + hydrogen
metal + chlorine ⟶ metallic chloride

All the common chlorides are readily soluble in water except three: silver chloride, mercurous chloride, and lead chloride. *The metals having insoluble chlorides do not react with the acid.*

104. Test for a Chloride. — The insolubility of silver chloride is used as a means of identifying soluble chlorides. If a solution of silver nitrate is added to a solution of a chloride, a white, curdy precipitate separates, which darkens in the light.

The separation of an insoluble solid in a liquid is called precipitation; the solid is called a precipitate.

chloride of a metal + silver nitrate ⟶
silver chloride (as a precipitate) + nitrate of the metal

$$NaCl + AgNO_3 \longrightarrow AgCl\downarrow + NaNO_3$$
$$ZnCl_2 + 2\,AgNO_3 \longrightarrow 2\,AgCl\downarrow + Zn(NO_3)_2$$

The addition of silver nitrate causes a white precipitate in many solutions other than those of chlorides. *Silver chloride, however, is insoluble in dilute nitric acid.* Therefore,

the addition of nitric acid is necessary to complete the test. As hydrochloric acid is a solution of *hydrogen chloride*, the silver nitrate test *together with the litmus test* serves to identify it.

105. Uses of Hydrochloric Acid. — Hydrochloric acid is used in the making of chlorides, in cleaning metals and in

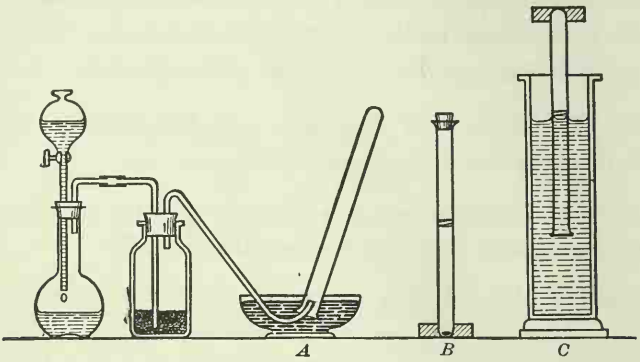


FIGURE 48.

This experiment shows that one volume of hydrogen is liberated by the action of sodium on two volumes of hydrogen chloride.

the manufacture of glue, gelatine, and glucose. Very small quantities of hydrochloric acid are found in the gastric juice and are necessary in gastric digestion. In medicine, very dilute hydrochloric acid is used in certain cases of indigestion.

106. Proportion of Hydrogen in Hydrogen Chloride. — When sodium is placed in hydrogen chloride, a violent reaction occurs, during which the sodium replaces the hydrogen. The reaction can be made less energetic by using sodium amalgam instead of sodium. Sodium chloride, mercury, and hydrogen result from the reaction. After the reaction, the volume of the hydrogen remaining is found to be one half that of the hydrogen chloride taken.

The experiment can be performed in the following manner: A glass tube is filled with the dry hydrogen chloride collected over mercury (Fig. 48, *A*).

Sodium amalgam is dropped into the tube and the mouth of the tube instantly closed with a stopper (Fig. 48, *B*). After the action is complete, the mouth of the tube is placed under some water in a tall cylinder, and the stopper removed (Fig. 48, *C*). Water rushes into the tube.

The remaining gas (hydrogen) is brought under atmospheric pressure by raising or lowering the tube in the cylinder until the liquid on the inside of the tube is at the same level as that outside. A small rubber band is then placed on the tube at the surface of the liquid.

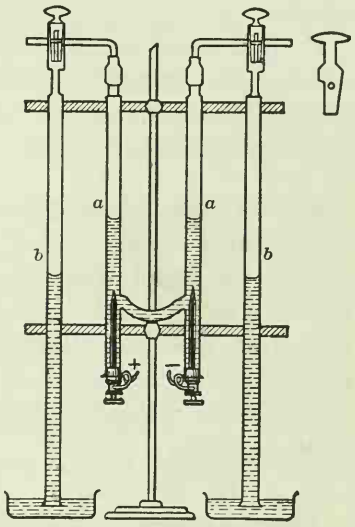


FIGURE 49.

This experiment shows that equal volumes of hydrogen and chlorine result from the electrolysis of concentrated hydrochloric acid.

The volume occupied by the hydrogen is found by measurement to be *one half of that occupied by the hydrogen chloride.* This experiment gives no data in regard to the proportion by volume occupied by the chlorine, hence the following experiment is necessary.

107. Relative Composition of Hydrogen Chloride. — The composition by volume can be shown by the use of the electrolysis apparatus shown in Figure 49. Hydrochloric

acid is placed in the tubes *a*. The current is turned on and allowed to pass through the solution, and the stopcocks are turned so that the hydrogen and chlorine will pass into the collecting tubes *b*. These tubes are filled with a saturated solution of common salt, in which chlorine is only slightly soluble.

Hydrogen is given off at the cathode and chlorine at the anode. The two collect at the same rate, showing that *equal volumes of hydrogen and chlorine are obtained by the electrolysis of hydrochloric acid.*

108. Volume Composition of Hydrogen Chloride. — By the sodium amalgam method, the volume of the hydrogen chloride was found to be twice the volume of the hydrogen. In the electrolysis of hydrogen chloride solution just described, we have shown that the volume of the hydrogen set free is equal to the volume of the chlorine. Hence we may represent the volumetric composition of hydrogen chloride by the equation:

$$\underset{\text{1 volume of hydrogen}}{H_2} + \underset{\text{1 volume of chlorine}}{Cl_2} \longrightarrow \underset{\text{2 volumes of hydrogen chloride}}{2\,HCl}$$

SUMMARY

Hydrogen chloride may be prepared: (1) by direct union of its elements; (2) by the action of sulphuric acid with a chloride. The latter is the common method.

It is a **gas** with a pungent odor. One liter under standard conditions weighs 1.64 grams. One liter of water at 20° dissolves 450 liters of hydrogen chloride.

The dry gas is inactive; its water solution is a typical acid. The replacement of the hydrogen of hydrochloric acid by a metal

gives a chloride. The chlorides of all but three of the common metals are soluble in water.

The test for a chloride is the formation with silver nitrate of a white curdy precipitate that is insoluble in nitric acid.

The chief **uses** of hydrochloric acid are for the preparation of chlorides, glucose, glue, and gelatine, and for cleaning metals.

Acids contain hydrogen that may be replaced by a metal. Their water solutions turn litmus red and usually have a sour taste.

A salt is a metal combined with an acid radical.

Two liters of hydrogen chloride, when decomposed, yield one liter of hydrogen and one liter of chlorine.

EXERCISES

1. Why is not the direct union of hydrogen and chlorine a convenient method of making hydrogen chloride?

2. How is hydrogen chloride collected and why is this method used?

3. Give a reason for the use of each substance employed in the laboratory preparation of hydrogen chloride.

4. State and explain the general method for preparing volatile acids.

5. Why is tin moistened with a solution containing hydrochloric acid before being soldered? Why cannot this acid be used with lead?

6. When chlorine is brought in contact with ammonia, which is a compound of hydrogen and nitrogen, a reaction occurs. Name one compound formed.

7. What products are formed when metallic magnesium is treated with hydrochloric acid?

8. What is formed when an amalgam of sodium and mercury is exposed to hydrogen chloride?

9. How would you determine whether or not a gas is hydrogen chloride?

10. State the difference between hydrogen chloride and hydrochloric acid.

11. Name two metals that replace hydrogen in dilute hydrochloric acid and two that do not.

12. What weight of sulphuric acid would be needed for a complete reaction with 117 grams of sodium chloride?

13. How many grams of sodium hydrogen sulphate would be formed by the reaction of 25 grams of sodium chloride with sulphuric acid?

14. Give three distinct characteristics of acids in water solution.

15. State the properties that cause hydrochloric acid to be called a typical acid.

16. What is a salt? A chloride? An acid?

17. How could you determine whether an unknown substance is a chloride? Whether it is hydrochloric acid?

18. Give the volume composition of hydrogen chloride and state how it is determined.

19. Write word equations for:

(*a*) the laboratory preparation of hydrogen chloride;

(*b*) the reaction of zinc with hydrochloric acid;

(*c*) the union of hydrogen with chlorine.

$$\underset{2+32+64}{H_2SO_4} + \underset{23+35.5}{NaCl} \longrightarrow HCl + NaHSO_4$$

$$\frac{x}{98} = \frac{117}{58.5}$$

$$58.5x = 117 \cdot 98$$

$$x = \frac{117 \cdot 98}{58.5}$$

$$x = 196 \text{ g}$$

Joseph Louis Gay-Lussac was born in 1778 in the old province of Limousin. In 1809, he became Professor of Chemistry at the École Polytechnique and at the same time was a professor of physics at the Sorbonne. In 1832, he resigned the latter position to take the chair of general chemistry at the Jardin des Plantes.

His researches on the combining volumes of gases resulted in the law that bears his name. This and his investigations on the relation between the volumes of gases and their temperatures, as well as those on iodine and cyanogen, have won enduring fame for him. Until his death in 1850, there was hardly a branch of the pure or applied chemistry of his time that Gay-Lussac did not illuminate by his numerous researches and clear explanations.

CHAPTER IX

MOLECULAR COMPOSITION

109. Volume Relation of Gases. — It has been shown in the volumetric synthesis of steam (§ 42) that

1 volume of oxygen unites with 2 volumes of hydrogen to give 2 volumes of steam.

We have also shown that

1 volume of chlorine unites with 1 volume of hydrogen to give 2 volumes of hydrogen chloride (§ 108).

The study of the action of other gases gives similar results; thus:

1 volume of nitrogen with 3 volumes of hydrogen gives 2 volumes of ammonia.

In these cases, the ratio of the volumes of the gases that combine can be expressed in whole numbers; this is also true of the ratio of the volume of each of the combining gases to the volume of the product.

110. Law of Gay-Lussac. — The relations stated in § 109 were first generalized by Gay-Lussac in his law of volumes: *The relative combining volumes of gases and the volume of the product, if gaseous, may be expressed by small whole numbers.* Two other generalizations relative to gases are:

Boyle's Law: the volume of any gas varies inversely as the pressure, if the temperature remains the same; and

Charles' Law: the volume of any gas varies directly as the absolute temperature, if the pressure remains the same.

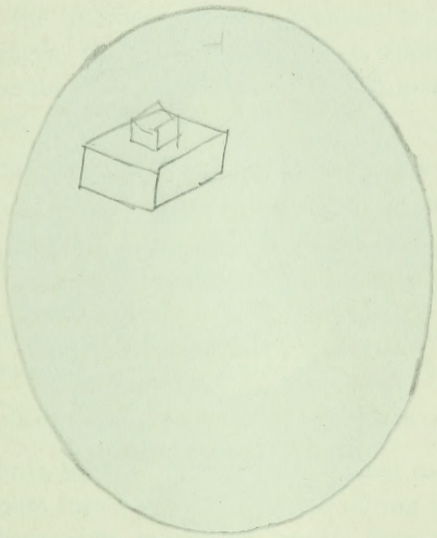
111. Avogadro's Hypothesis. — These uniformities in the behavior of gases led Avogadro in 1811 to make the following hypothesis: *Equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.* That is to say, a liter of hydrogen contains just *as many molecules* as a liter of oxygen, a liter of chlorine, a liter of hydrogen chloride, or a liter of any other gas measured under the same conditions of temperature and pressure. This general statement, while still regarded as a theory or hypothesis, proved of great value in the development of chemistry. By means of it chemists were first able to decide what formulas to use in representing chemical compounds.

The actual number of molecules in a liter of any gas is very great, but we have no concern with the actual number. We know nothing whatever of the number of molecules in equal volumes of solids or of liquids. It is probable that in them molecules, as such, do not exist.

112. Number of Atoms in Molecules of Gaseous Elements. — If we knew the number of atoms of each element in a molecule, we could determine the relative weight of the atoms. We cannot count the number of atoms in a molecule, but by means of Avogadro's hypothesis we can arrive at a definite *belief* in the matter.

Experiment shows that *one* volume of chlorine and *one* volume of hydrogen combine to form *two* volumes of hydrogen chloride.

1 volume of hydrogen + 1 volume of chlorine
$\longrightarrow$ 2 volumes of hydrogen chloride



Amadeo Avogadro, an Italian scientist, was born in 1776 and died in 1856 while he was Professor of Physics at Turin. He enunciated the hypothesis that bears his name and thus laid the foundation for determining the number of atoms in a molecule of an elementary gas. Avogadro showed the relation between the law of Gay-Lussac and the atomic hypothesis of Dalton. He assumed that the molecule of an elementary gas could be composed of smaller units, and that by this assumption the relative densities of gases could be made to agree with the values determined by experiment.

Suppose the given volume of hydrogen contains 1000 molecules, then, by Avogadro's hypothesis, 1000 molecules must also be contained in an equal volume of chlorine; and likewise, since the hydrogen chloride occupies *twice* the space of the hydrogen, the volume of hydrogen chloride resulting from the combinations must contain 2000 molecules. Or, briefly stated:

1000 molecules of hydrogen + 1000 molecules of chlorine
$\longrightarrow$ 2000 molecules of hydrogen chloride

1 molecule of hydrogen + 1 molecule of chlorine
$\longrightarrow$ 2 molecules of hydrogen chloride

In each of these two molecules of hydrogen chloride, there must be some hydrogen, at least *one* atom (cf. § 73).

$\therefore$ 1 molecule of hydrogen $\longrightarrow$ at least 2 atoms of hydrogen.

In other words, the experiment indicates that each hydrogen molecule splits into *at least* two parts during the chemical action. These parts cannot be smaller than atoms, since atoms are not divided during a chemical change. Consequently, each hydrogen molecule contains *at least two* atoms of hydrogen. Similar reasoning shows that the *chlorine molecule* also contains *at least two atoms.*

It is to be noted that *any even number* might be used instead of two, but since there is no chemical action known in which either the hydrogen or the chlorine molecule seems to divide into more than two parts, it is not probable that there are more than two atoms in either of these molecules.

Let us consider the composition of steam. Experiment shows that *two* volumes of hydrogen unite with *one* volume of oxygen, to yield *two* volumes of steam. Assuming 1000 molecules to a volume, and reasoning according to Avogadro's

hypothesis, the two volumes of hydrogen and of steam must each contain 2000 molecules. Then:

2000 molecules of hydrogen + 1000 molecules of oxygen
$\longrightarrow$ 2000 molecules of steam

In each of these 2000 molecules of steam, there must be *at least one* atom of oxygen.

Not less than 2000 atoms of oxygen, therefore, have been obtained from the 1000 molecules of oxygen. Consequently, each oxygen molecule contains *at least two atoms* of oxygen. This experiment would indicate that 1 molecule of steam contains 1 molecule of hydrogen, but it has been already shown that the hydrogen molecule contains at least two atoms. The steam molecule, then, must contain at least one oxygen atom and two hydrogen atoms. The above experiments and logical deductions show why the formula of hydrogen is written as H_2, that of chlorine as Cl_2, that of oxygen as O_2, and that of water (steam) as H_2O.

While the molecules of most common gaseous elements contain two atoms, this is not true of all elements in the gaseous state. For example, argon, mercury, zinc, and helium have each one atom to the molecule; phosphorus has four; and sulphur eight, six, or two, according to the temperature.

SUMMARY

Uniformities in the Behavior of All Gases.

Boyle's Law: The volume of any gas varies inversely as the pressure, if the temperature remains the same.

Charles' Law: The volume of any gas varies directly as the absolute temperature, if the pressure remains the same.

Gay-Lussac's Law: The relative combining volumes of gases

and the volume of the product, if gaseous, may be expressed by small whole numbers.

The **uniformities in the behavior** of all gases, independent of their chemical composition, lead to the belief that **equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules.** (Avogadro's hypothesis.)

It follows from Avogadro's hypothesis, and from the volumetric composition of these gaseous compounds, that the elements hydrogen, oxygen, chlorine, and nitrogen each have **two** atoms to the molecule. In the gaseous state, zinc and mercury have **one** atom to the molecule; phosphorus has **four.**

EXERCISES

1. What uniformities (laws) are known about the physical and chemical behavior of gases?

2. What are the evidences in support of Avogadro's hypothesis?

3. Show how Gay-Lussac's Law of Volumes applies to the union of hydrogen and chlorine.

4. Show by Gay-Lussac's Law that there always must be some oxygen left when you attempt to combine two and three tenths volumes of hydrogen with an equal volume of oxygen.

5. One liter of marsh gas in burning combines with two liters of oxygen. How many molecules of oxygen are needed for the complete combustion of one molecule of marsh gas?

6. Approximately what are the relative numbers of molecules of oxygen and nitrogen in air?

7. What volume of *air* is needed for the complete combustion of 100 c.c. of marsh gas?

8. Two molecules of nitric oxide (gas) unite with one molecule of oxygen when the two are brought together. How many cubic centimeters of oxygen would be needed for com-

plete reaction with 64 c.c. of nitric oxide? How much air would be needed for the same purpose?

9. Give reasons for believing that the oxygen molecule contains at least two atoms.

10. One volume of hydrogen unites with one volume of bromine gas, forming two volumes of hydrogen bromide. How many atoms are there in the molecule of gaseous bromine? Explain.

11. Two tanks of equal capacity contain oxygen. The gas in the first is under atmospheric pressure; that in the second is under 3.2 atmospheres pressure. How does the weight of oxygen in the second tank compare with the weight of that in the first? (Boyle's Law will point the way to the solution of this problem.)

12. When two volumes of hydrogen chloride are decomposed by sodium amalgam, they yield one volume of hydrogen. Assuming 3000 molecules to one volume, show how Avogadro's hypothesis can be used to indicate the composition of the hydrogen molecule.

CHAPTER X

ATOMIC AND MOLECULAR WEIGHTS

113. Atomic Weights. — Some atoms are heavier than others. An atom of mercury weighs two hundred times as much as an atom of hydrogen and about twelve and a half times as much as an atom of oxygen.

The atomic weight of an element is a number that expresses the weight of one atom of that element compared with the weight of one atom of oxygen, taken as 16.

The weight of the oxygen atom was placed at 16 because oxygen enters into direct combination with most elements, and 16 is the smallest whole number that can be assigned to the oxygen atom and have the atomic weight of hydrogen, the lightest element, not less than 1.

114. Atomic Weight of Hydrogen. — Since it has been shown that there are twice as many hydrogen atoms as oxygen atoms in one molecule of steam (§ 113), and since the oxygen in water weighs 7.9365 times as much as the hydrogen, we can now calculate the weight of the hydrogen atom as compared with the weight of the oxygen atom.

The steps of the argument are as follows:

(*a*) The oxygen in steam is 7.9365 times as heavy as the hydrogen.

(*b*) There cannot be less than one atom of oxygen in the steam molecule.

(*c*) The weight of the oxygen atom is taken as 16.

(*d*) Therefore the weight of all the hydrogen in the steam molecule is $\frac{16}{7.9365} = 2.016$.

(*e*) But we have shown that there are two hydrogen atoms for each oxygen atom in the molecule of steam.

Conclusion: The atomic weight of hydrogen is

$$\frac{2.016}{2} = 1.008.$$

115. Determination of Molecular Weights.—Suppose that a large number of balls are made of iron, another lot of balls of the same size are made of aluminum, and that one of the iron balls weighs 3 times as much as one of the aluminum balls. Since one iron ball weighs 3 times as much as one aluminum ball, ten, twelve, two hundred, or any number of iron balls must weigh 3 times as much as the same number of aluminum balls. One pound of aluminum would make as many balls as three pounds of iron. Chemists use a similar course of reasoning when thinking about the molecules of a substance. One molecule of hydrogen is like every other molecule of hydrogen, and one molecule of oxygen is like every other molecule of oxygen. Each molecule of hydrogen and each molecule of oxygen contains two atoms. The weight of the hydrogen molecule is represented by the number 2.016, and the weight of the oxygen molecule by the number 32. We reason, therefore, that there are as many molecules in 2.016 grams of hydrogen as there are in 32 grams of oxygen.

Avogadro's hypothesis states that equal volumes of all gases, when measured under like conditions, contain the same number of molecules, or, in other words, the molecules of one gas occupy the same space as an equal number of molecules

Theodore W. Richards (1868–1928) was an eminent American chemist. For many years he was Professor of Chemistry at Harvard. His revisions of the atomic weights of more than a score of elements were accorded world-wide recognition and in 1916 he was awarded the Nobel prize in chemistry. His later researches dealt with atomic volumes and the compressibility of atoms.

Edward W. Morley was born in 1838 at Newark, New Jersey. He graduated at Williams and in 1869 became Professor of Chemistry in Western Reserve University.

He has explored fields in both physics and chemistry. His greatest achievement was the determination of the exact ratio by which oxygen and hydrogen combine by weight, as this ratio has been generally accepted.

of any other gas. Therefore, 2.016 grams of hydrogen occupy the same space as 32 grams of oxygen. If this is true, it is an easy matter to calculate the space occupied by 2.016 grams of hydrogen or 32 grams of oxygen. An increase in temperature, however, or a decrease in pressure, causes the volume of a gas to increase, if the gas is free to expand. Because of this fact, scientists compare weights of equal volumes at what are known as *standard conditions*. A gas is at standard conditions when its temperature is 0° C. and it is under a pressure equal to that exerted by a column of mercury 760 millimeters high (Chapter XL). One liter of oxygen at standard conditions weighs 1.429 grams. Therefore the number of liters in 32 grams of oxygen, at standard conditions, is 32 ÷ 1.429, or 22.4 liters.

One liter of hydrogen at standard conditions weighs 0.09 gram. The volume occupied by 2.016 grams of hydrogen is 2.016 ÷ 0.09, or 22.4 liters.

A *gram-molecular weight* (mole) of any substance is a weight in grams that is numerically equal to the molecular weight of that substance. 32 grams of oxygen is a gram-molecular weight, or *mole* of oxygen, and 2.016 grams of hydrogen is a gram-molecular weight, or mole of hydrogen. The molecular weight of carbon dioxide is 44, so 44 grams is a gram-molecular weight of carbon dioxide. Now we have shown that 32 grams of oxygen and also 2.016 grams of hydrogen, that is, a gram-molecular weight of either of these gases, occupies 22.4 liters, and, by a similar course of reasoning, it might be shown that a gram-molecular weight of *any* gas, at standard conditions, occupies 22.4 liters. 22.4 liters is the *gram-molecular volume* of any gas (Fig. 50). When gases are actually weighed, the results agree closely with this deduction.

The gram-molecular weight and the gram-molecular volume are of use in two important kinds of calculation:

(1) We can calculate the weight of 1 liter of any gas by dividing its gram-molecular weight by 22.4. (2) We can find the molecular weight of any gas, provided we know the weight of 1 liter.

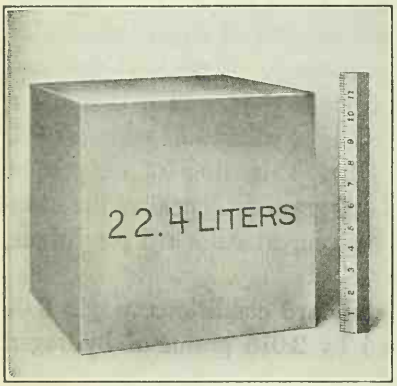


FIGURE 50.

No matter what gas we put into this box, the weight of the gas (in grams) is numerically equal to the molecular weight of the gas.

Thus, 1 liter of marsh gas (CH_4) weighs 0.716 g. Multiplying this value by 22.4, we get 16.04. This corresponds very closely to the molecular weight calculated from the formula. If 82 c.c. (0.082 liter) of carbon dioxide weigh 0.1611 gram, we can find the weight of 22.4 liters of carbon dioxide by the proportion:

$$0.082 \text{ liter} : 22.4 \text{ liters} :: 0.1611 \text{ gram} : x \text{ grams}$$
$$x = 44 \text{ grams}$$

Therefore, the molecular weight of carbon dioxide is 44.

In determining the formula of a compound the *weight* of its molecules is a decisive factor. We see from the above paragraphs how, by merely weighing a gas carefully, we can easily decide what one of its molecules weighs in comparison with an oxygen atom taken as 16.

116. Density and Specific Gravity. — *The density of a substance is its weight per unit volume.* In the cases of

liquids and solids, scientists usually take one gram as the unit of weight, and one cubic centimeter as the unit of volume. The density of a liquid or solid, then, is the number of grams of that substance occupying one cubic centimeter. The density of a gas is often considered to be the weight of one liter of that gas measured at standard conditions, thus, the density of hydrogen is 0.09 gram per liter. In stating the density of a substance, the unit of weight and the unit of volume must be named.

Density should not be confused with specific gravity. *Specific gravity is the weight of a volume of a substance compared with the weight of an equal volume of the particular substance taken as a standard.* In the case of liquids and solids, water is the standard for specific gravity. The statement, "The specific gravity of aluminum is 2.72," means that aluminum weighs 2.72 as much as an equal volume of water. Air, at standard conditions, is the common standard for the specific gravity of gases. The specific gravity of hydrogen chloride is 1.24; this means that hydrogen chloride is 1.24 times as heavy as air, both gases being weighed under the same conditions.

The density of air at standard conditions is 1.293 grams per liter. 22.4 liters of air weigh 1.293 g. $\times$ 22.4, or 28.96 g., nearly 29 grams. Since a gram-molecular weight of any gas is the weight of approximately 22.4 liters of that gas, its specific gravity can be calculated by dividing the gram-molecular weight by 29 grams, the weight of 22.4 liters of air. A gas having a molecular weight less than 29 is lighter than air; a gas having a molecular weight more than 29 is heavier than air.

Because the specific gravity of a gas is equal to its molecular weight divided by 29, the molecular weight of a gas is

equal to its specific gravity multiplied by 29. This fact is of use in calculating the specific gravity of a gas from its molecular weight, or the molecular weight from the specific gravity, but the answers obtained are only approximately correct.

The term *vapor density* is sometimes used in calculating molecular weights. The vapor density of a gas is its specific gravity with hydrogen as a standard. Since the molecular weight of hydrogen is approximately 2, *the molecular weight of any gas* can be obtained by multiplying its vapor density by 2. To get the approximate weight of a liter of any gas, we multiply the weight of 1 liter of hydrogen (0.09 gram) by the vapor density.

117. Problems Involving Volumes of Gases. — In an equation such as

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

it will be seen that coefficients used to balance equations indicate gram-molecules. In case of gases, these coefficients also indicate *gram-molecular volumes.*

Problems involving *volume only* are simple to solve, because the relation between the number of molecules of the gases represented in the chemical equation is the same as the relation between the volumes of these gases (§ 111), *so the coefficients represent the relative volumes of the gases.*

Problem. When marsh gas, CH_4, burns, carbon dioxide and water are formed. How many liters of oxygen will be required to burn 10 liters of marsh gas?

$$\begin{array}{ccccc} 10 \text{ liters} & & x \text{ liters} & & \\ CH_4 & + & 2\,O_2 & \longrightarrow & 2\,H_2O + CO_2 \\ 1 \text{ volume} & & 2 \text{ volumes} & & \end{array}$$

1 vol. : 2 vol. : : 10 liters : x liters

x = *20 liters of oxygen. Answer.*

Problems involving relations between the weights of substances and the volumes of gases concerned in a reaction can be solved directly by making use of the gram-molecular volume.

Problem. How many liters of hydrogen would be needed to reduce 100 grams of magnetic oxide of iron (Fe_3O_4)?

$$\begin{array}{ccccc} 100 \text{ grams} & & x \text{ liters} & & \\ Fe_3O_4 & + & 4\,H_2 & \longrightarrow & 3\,Fe + 4\,H_2O \\ 168 + 64 & & 4 \times 22.4 & & \\ 232 & & 89.6 & & \end{array}$$

$$232 : 89.6 :: 100 \text{ grams} : x \text{ liters}$$

$$x = 38.6 \text{ liters.} \quad \textit{Answer.}$$

In any type of problem, x may be on either side of the arrow, and the known weight may also be on either side of the equation. Knowing the volume of a gas, the weight of any substance in the equation may also be calculated. If the weight of a liter of the gas is given or can be calculated (§§ 115, 116), then the weight of the gas may be found by multiplication, and the problem solved as a weight problem.

SUMMARY

The atomic weight of an element is the weight of one of its atoms compared with 16, the number chosen as the weight of 1 atom of oxygen.

A gram-molecular weight, or mole, of a substance is a weight in grams numerically equal to the molecular weight of that substance. **The gram-molecular volume** of any gas is 22.4 liters.

The molecular weight of a gas can be computed approximately from the weight of any volume of the gas by calculating the weight of 22.4 liters at standard conditions.

The weight of 1 liter of a gas is approximately equal to its gram-molecular weight divided by 22.4.

Density is weight per unit volume.

The specific gravity of a liquid or of a solid is the number of times the substance is as heavy as an equal volume of water.

The specific gravity of a gas is the number of times the gas is as heavy as an equal volume of air, both measured under the same conditions.

The specific gravity of a gas is approximately equal to its **molecular weight divided by 29.**

The molecular weight of a gas is approximately equal to its specific gravity multiplied by 29. Gases having molecular weights less than 29 are lighter than air; those having molecular weights more than 29 are heavier than air. The molecular weight of a gas is also found by multiplying its vapor density by 2.

Relative volumes of gaseous substances are represented by the coefficients of their molecules in an equation.

EXERCISES

1. A liter of bromine gas, at standard conditions, would weigh 7.135 grams. What is the molecular weight of bromine? Using the answer to Question 10, Chapter IX, determine the atomic weight of bromine.

2. A liter of marsh gas, at standard conditions, weighs 0.716 gram. What is the molecular weight of marsh gas? This gas is composed of carbon 75%, hydrogen 25%. What part of the molecular weight is carbon? What part is hydrogen? The atomic weight of carbon is 12. How many atoms of each element are there in one molecule of marsh gas?

3. What is the weight at standard conditions of 1 c.c. of hydrogen? Of 150 c.c.?

4. 130 c.c. of a certain gas at standard conditions weigh 0.35 g. What is the weight of one liter? What is the specific gravity of the gas?

5. 164 c.c. of hydrogen chloride weigh 0.267 g., standard conditions. From this fact, find (*a*) the molecular weight of the gas; (*b*) the weight of one liter; (*c*) the specific gravity.

6. What is the vapor density of ozone, if 325 c.c. of this gas at standard conditions weigh 0.702 g.? What is its molecular weight?

7. 0.58 gram of acetylene gas has a volume of 499.4 c.c., standard conditions. What is the molecular weight of acetylene? What is its specific gravity?

8. 150 c.c. of ammonia weigh 0.5397 times as much as 150 c.c. of oxygen. Give reasoning to show that one molecule of ammonia weighs 0.5397 times as much as one molecule of oxygen.

9. The specific gravity of nitrogen is 0.9674. The specific gravity of oxygen is 1.1054. One liter of oxygen weighs how many times as much as one liter of nitrogen? Calculate the weight of one liter of nitrogen. Determine the molecular weight of nitrogen.

10. One liter of nitrogen unites with two liters of oxygen to form two liters of nitrogen peroxide. How many molecules of oxygen unite with one molecule of nitrogen? How many molecules of nitrogen peroxide are formed?

11. Oxygen and nitrogen molecules each contain two atoms. Making use of the answers in Question 10, determine the number of atoms of nitrogen and oxygen in one molecule of nitrogen peroxide.

12. The oxygen in nitrogen peroxide weighs 2.284 times as much as the nitrogen. Using the answer to Question 11, find how many atoms of oxygen weigh 2.284 times as much as one atom of nitrogen. What is the atomic weight of oxygen? What number represents the total weight of the oxygen atoms in nitrogen peroxide? What is the atomic weight of nitrogen?

13. 230 c.c. of ether vapor, corrected to standard conditions, weigh 0.76 g. What is the molecular weight of ether?

14. The specific gravity of ammonia is 0.597. What is its molecular weight?

15. The molecular weight of carbon monoxide is 28. What is its specific gravity?

16. The molecular weight of sulphur dioxide is 64. What is its vapor density? What is the weight of one liter of sulphur dioxide?

17. The vapor density of cyanogen is 26. What is its molecular weight? The weight of one liter?

18. State the relative volumes of each gaseous substance indicated by the equations representing:

(*a*) hydrogen combining with chlorine;
(*b*) chlorine combining with water;
(*c*) hydrogen combining with bromine.

19. 30 c.c. of hydrogen are mixed with 40 c.c. of air that contains 20% of oxygen, and the mixture is ignited. What gases remain after explosion, and what is the volume of each? All gas volumes in this question are measured at the same temperature and pressure.

20. How many volumes of oxygen are required to burn one volume of methane (CH_4) to carbon dioxide and water?

CHAPTER XI

ELECTRONS AND VALENCE

118. Puzzling Things about Atoms. — Lord Kelvin, shortly before his death in 1907, expressed regret that after fifty years of devotion to science, he was still ignorant of the cause of chemical action. A new and startling development in chemical theory was just about to begin. To-day a schoolboy may readily understand what the greatest scientist of his time could not know, for the patient researches of earnest workers into the world of the unseen have revealed many things about atoms. The totality of this work probably represents one of the greatest achievements of the human mind, and shows what may result when great observing power is coupled with a vigorous imagination.

The new theories explain not only what Kelvin wondered about, but several other puzzling things. They tell us why some elements are metals and some non-metals; why some elements are very active chemically, some comparatively inactive, and why a few of the elements refuse entirely to enter into combination. We can explain why metals conduct electric currents, and why non-metals do not; what takes place in a radio tube; by what process electroplating is accomplished, and how batteries produce electric currents. Some of the experiments show cases in which one element is converted into another.

One matter in particular has long been a mystery to chemists. It concerns what is called *valence*, a matter to be explained here in detail. We find formulas such as HCl

(hydrogen chloride), H_2O (water), CH_4 (marsh gas), and Fe_2O_3 (iron oxide). These show that all atoms do not have the same capacity for holding each other in chemical combination. Chlorine holds only one hydrogen atom, while oxygen can hold two, and carbon four; two iron atoms can hold three oxygen atoms. It was seen long ago that there are rules in such combinations, but their *why* was not known until lately.

119. Matter is Nothing but Electricity. — A statement like this, though made only as a theory, requires proof. It has long been known that when almost any two non-conducting substances, such as glass and silk, or hair and rubber, are rubbed together, both objects become electrically charged, one positively, the other negatively. It is also known that particles of negative electricity are thrown off from the cathode of an X-ray tube, no matter what metal is used. Further, many substances that are electrically neutral, on being dissolved in water, separate into two or more kinds of particles, each of which bears either a positive or a negative charge. In all of these examples we have electric charges produced, and in none of them is there any source of the electricity except the substances concerned. Such facts alone would make us think that all matter must be made up partly of electricity.

The name of the new belief is the *electron theory of the atom.* Prominent chemists and physicists are now busy with further investigation in the field, and additional and more accurate information may be expected with some confidence. But already we have enough foundation to warrant the use of the new hypothesis as an aid in understanding chemical actions.

120. Radioactivity. — Becquerel discovered that uranium, one of the very heavy elements, shoots off particles which have electrical properties. One of his pupils, Madame Curie, found in the mineral from which uranium is obtained, a new element, another rare metal, which she named *radium*. She separated a little of a compound of this metal from several tons of the ore, and discovered that it constantly gave off negative particles of electricity, as well as two other kinds of radiations. Radium atoms, for some reason not yet understood, decompose at a slow rate, spontaneously and constantly. It was found that the element helium is one of the products of the atomic decompositions of radium. Madame Curie and other scientists working with the new metal came to the conclusion that its atoms are composed of positive and negative electricity, and of nothing else.

These discoveries set chemists and physicists thinking about atoms and experimenting with them in a way that had never before been possible. The facts, when put together, led to the conclusion that atoms of all elements are made up of nothing but positive and negative electricity.

121. Moseley and Atomic Numbers. — Our knowledge of the way in which atoms are built up of the two kinds of electricity is due chiefly to a young Englishman named Moseley. He directed X-rays at crystals, and found a law, or regularity, in the effect produced that depends on the number and arrangement of electrical particles in the elements present (see § 524). He arranged the elements accordingly, giving to each an atomic number, indicating its order in the list. In this list the atomic number of hydrogen is 1, that of helium 2, lithium 3, and so on as shown in the table on the next page. Strangely enough,

this order agreed almost exactly with that suggested years before by Mendelejeff, a Russian, who considered nothing but atomic weights in making his table. In both cases, but more strikingly in Moseley's list, the arrangements showed a remarkable repetition of chemical properties in groups or periods. Moseley's work showed a decided connection between the structure of atoms and their chemical properties.

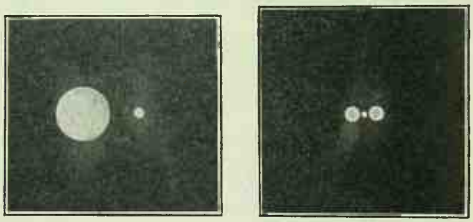
ELEMENTS ARRANGED IN THE ORDER OF THEIR ATOMIC NUMBERS

1.	Hydrogen	H	28.	Nickel	Ni	55.	Cæsium	Cs
2.	Helium	He	29.	Copper	Cu	56.	Barium	Ba
3.	Lithium	Li	30.	Zinc	Zn	57.	Lanthanum	La
4.	Glucinum	Gl	31.	Gallium	Ga	58.	Cerium	Ce
5.	Boron	B	32.	Germanium	Ge	59–72.	Rare Earth Elements	
6.	Carbon	C	33.	Arsenic	As			
7.	Nitrogen	N	34.	Selenium	Se			
8.	Oxygen	O	35.	Bromine	Br	73.	Tantalum	Ta
9.	Fluorine	F	36.	Krypton	Kr	74.	Tungsten	W
10.	Neon	Ne	37.	Rubidium	Rb	75.	. . . . .	
11.	Sodium	Na	38.	Strontium	Sr	76.	Osmium	Os
12.	Magnesium	Mg	39.	Ytterbium	Yt	77.	Iridium	Ir
13.	Aluminum	Al	40.	Zirconium	Zr	78.	Platinum	Pt
14.	Silicon	Si	41.	Cerbium	Cb	79.	Gold	Au
15.	Phosphorus	P	42.	Molybdenum	Mo	80.	Mercury	Hg
16.	Sulphur	S	43.	. . . . .		81.	Thallium	Tl
17.	Chlorine	Cl	44.	Ruthenium	Ru	82.	Lead	Pb
18.	Argon	A	45.	Rhodium	Rh	83.	Bismuth	Bi
19.	Potassium	K	46.	Palladium	Pd	84.	Polonium	Po
20.	Calcium	Ca	47.	Silver	Ag	85.	. . . . .	
21.	Scandium	Sc	48.	Cadmium	Cd	86.	Radon	Rn
22.	Titanium	Ti	49.	Indium	In	87.	. . . .	
23.	Vanadium	V	50.	Tin	Sn	88.	Radium	Ra
24.	Chromium	Cr	51.	Antimony	Sb	89.	Actinium	Ac
25.	Manganese	Mn	52.	Tellurium	Te	90.	Thorium	Th
26.	Iron	Fe	53.	Iodine	I	91.	Uranium X	UX_2
27.	Cobalt	Co	54.	Xenon	Xe	92.	Uranium	U

122. Atoms Are Composed of a Nucleus and Outside Electrons. — The electron theory says that all atoms are composed of two parts. In the center is a nucleus, made up of both positive and negative charges, but with the posi-

tive always present in the greater number. Around this nucleus are negative particles in a number sufficient to balance the excess positive charges of the nucleus, so that the atom as a whole is electrically neutral. Positive particles are known as *protons*, and the negative particles as *electrons*.

Thus the hydrogen atom, the simplest of all, has one excess positive particle, or proton, in its nucleus. This is balanced by one electron. It is this fact which puts hydrogen first in the list of elements according to atomic numbers. The atomic number of hydrogen is 1. Helium has a nucleus with two excess protons, and has two outside electrons. Its atomic number consequently is 2. Lithium has a nucleus with three excess protons, and these are balanced by three outside electrons. The atomic number of lithium is 3.



Hydrogen Atom Helium Atom

FIGURE 51.

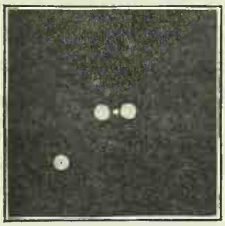
The small dot in each picture represents the nucleus. Hydrogen has one electron outside the nucleus, helium has two. For a complete first ring two electrons are needed; hence helium is inert, while hydrogen is active.

The atomic number of an element is equal to the number of electrons outside the nucleus of its atom.

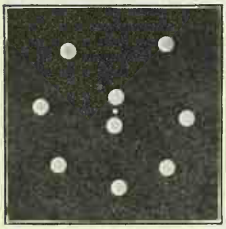
The electrons probably rotate in orbits about the nucleus. We shall speak of them here as if they were grouped in rings.

123. Outside Electrons Determine Chemical Properties. — Irving Langmuir, an American chemist, was the first to show that there is a definite arrangement of the outside

electrons in an atom. They appear to exist in groups or rings about the nucleus. If there are either one or two electrons, they are found in a first ring. If more than two, they are found in additional rings. Eight are required to complete a second ring, eight more for a third; other rings each require eighteen electrons. The chemistry of an element depends on whether the outer ring is filled or not.



Lithium Atom



Fluorine Atom

FIGURE 52.

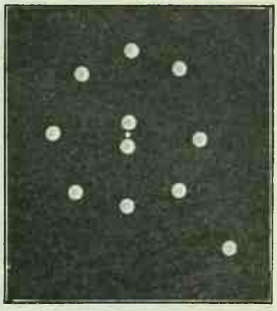
Both atoms have incomplete second rings. If lithium lends to fluorine there are eight electrons to make one complete second ring.

Thus hydrogen, with its one free electron (Fig. 51), has not enough to fill even the first ring; helium (Fig. 51), atomic number 2, has the necessary number, two. Now we note a great difference in the chemistry of the two elements. Hydrogen combines readily with many other elements, while helium refuses absolutely to enter into any chemical combination. The theory explains these facts on the ground that hydrogen has an incomplete ring, while helium has one that is satisfied.

Lithium (Fig. 52), atomic number 3, has the two electrons necessary for the first ring, and *one besides*. We should, therefore, expect lithium to enter into chemical action, not to be inactive like helium. This is the fact, for lithium is one of the most active of the metals. Fluorine (Fig. 52), atomic number 9, has the two electrons for the first ring, and seven, which is almost but not quite the necessary number, for the second ring. We should expect fluorine to be active, not inert. This agrees with experimental evi-

dence; fluorine is the most active non-metal known. It combines with both hydrogen and lithium, forming compounds which have the formulas HF and LiF.

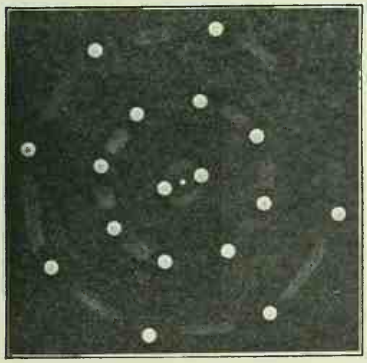
Sodium (Fig. 53), atomic number 11, has two electrons for the first ring, eight for the second, and one left over for the third. As far as the outer ring is concerned, sodium is thus in much the same condition as lithium. Facts show that sodium is very much like lithium both in chemical and physical behavior. Both are very active metals. It seems, therefore, that the single electron that each has in its outer ring has much to do with making the properties of two elements so much alike.



Sodium Atom

FIGURE 53.

Complete first and second rings, but only one lonely electron for the third ring. This element is a lender — a *metal.*

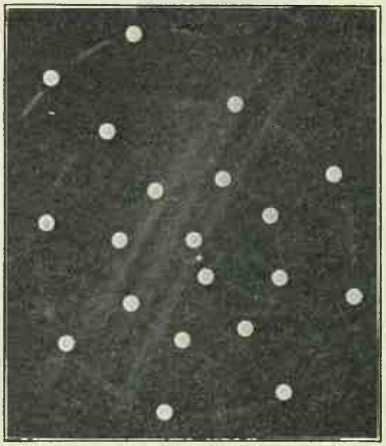


Chlorine Atom

FIGURE 54.

Almost enough electrons for three complete rings. One more is needed; so the element is a borrower — a *non-metal.*

Chlorine (Fig. 54), atomic number 17, has two electrons for the first ring, eight for the second, and seven towards forming the third. This makes the situation in its outer ring identical with that of fluorine. We should guess at this point that chlorine would resemble fluorine in its properties. Here again we have verification; the

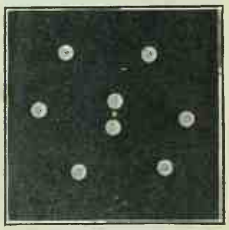


Calcium Atom
FIGURE 55.

Only two electrons for the fourth ring; the atom is therefore a lender rather than a borrower. Its valence is + 2.

two elements have been regarded for many years as members of a chemical family known as the *halogens*.

124. Metals and Non-metals. — While lithium and sodium are much like each other, they are entirely different from fluorine and chlorine. From what we have already said, this difference would be expected, for each of the two metals has only one free electron in its outer ring, while each of the two non-metals has seven. Calcium (Fig. 55), atomic number 20, has only two electrons in its outer ring; it resembles lithium and sodium much more than it does fluorine or chlorine because it has comparatively few electrons in its outer circle. Oxygen (Fig. 56), atomic number 8, has six electrons in its second ring. This makes it more like fluorine than like lithium, because it has almost enough electrons for a complete ring of eight. These illustrations serve to show a general fact; atoms with few electrons in the outer circle are metals; those with nearly eight electrons are non-metals.



Oxygen Atom
FIGURE 56.

Here we have an atom with a valence of − 2. It needs two electrons to make a complete second ring.

It further appears that when a small number of electrons are left for the outer circle, these are held very loosely. For example, electric currents, which are now known through these same theories to be streams of electrons, flow readily through metals, but only slightly through non-metals. It is believed that metal atoms shift their electrons one to the other, somewhat as buckets of water are passed from one person to the next by a line of men in putting out a fire in the country. If this is the case, the electrons of metals must be loosely held.

125. Electrons May Be Borrowed and Lent. — We have now to show why hydrogen combines readily with such elements as fluorine, chlorine, and oxygen, and why metals generally enter into chemical action with non-metals. Hydrogen has one electron in its first ring, not enough for completeness. Fluorine has seven, also not enough for completeness. But the hydrogen by lending its one electron to fluorine enables it to complete a second ring of eight electrons. Hence the compound hydrogen fluoride, HF, is readily formed.

Oxygen needs two electrons for completeness. Hence we should predict that the lending power of *two* hydrogen atoms would be necessary to secure the complete eight, and the formula of water, H_2O, is thus explained. We should expect also that lithium would be far more apt to lend its one free electron to fluorine or chlorine than to sodium which is, like lithium, a lender. These predictions agree with the experimental facts. We should expect one calcium atom, with its two extra electrons, to lend them to oxygen, which needs just this number. This, too, is an experimental fact; the formula of calcium oxide is CaO.

The behavior of atoms in chemical action is like what happens when groups of boys go to a field to play games. Two groups might arrive, neither of which had just the number of boys needed for the game; one might have too many, the other too few. By borrowing and lending, the numbers might be adjusted so that games could go on as desired. It appears that the metals, with their loosely-held, comparatively few outer electrons are willing lenders to the non-metals, which already have almost the necessary number to play the chemical games which nature decrees. Thus chemical action is explained.

126. Valence Depends on the Electrons in the Outer Ring. — It now begins to appear why varying numbers of different atoms are needed for chemical combination. It all depends on how many electrons are required by the borrowing element and on how many are available for lending by the other. Knowing the atomic number of an element, one can easily determine its combining power; experimental evidence confirms the results especially well for the first twenty or so elements. Above this number there is less certainty, owing to present lack of complete information concerning electrons in the fourth and later rings.

For example, suppose we wish to find the value for aluminum, whose atomic number is 13. Subtracting two for the first ring, and eight for the second, we have three left. This is less than half of the necessary eight. It is clear that aluminum is a metal and that it has three electrons for lending purposes. The valence of aluminum is said to be $+3$. Sulphur has an atomic number 16; subtracting, as before, two and eight, we find six electrons left for the outer ring. Evidently this element is a non-metal, for it needs to borrow

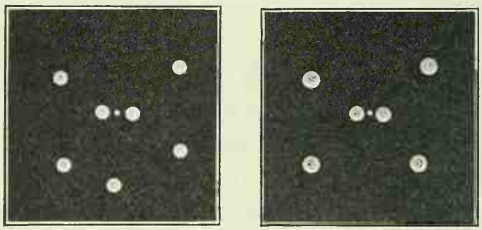
two electrons to secure a complete ring. Its valence is said to be − 2. The plus and minus signs indicate whether the element is a lender or a borrower; or, in other words, whether it is a metal or a non-metal.

The valence of an element is a number which indicates either (*a*) *the number of electrons it can lend as a metal, or* (*b*) *the number it can borrow as a non-metal.*

127. Atomic Weight Depends Chiefly on the Nucleus. — So far we have said very little about the nuclei of the atoms. The reason is that the chemistry of the elements depends almost wholly on the free electrons; it is the outer ring which determines whether the element is a metal, or a non-metal, whether it is active or inactive chemically, and what the valence is. The weight of an atom, however, depends largely on the nucleus, which, as we have already said, is made up of both positive and negative particles. With one or two exceptions, the arrangement of elements, when listed according to atomic weight, is identical with that obtained when they are listed according to atomic numbers.

Isotopes. — It has been discovered that we may have two kinds of atoms, alike in respect to the numbers of electrons outside the nucleus, but different as to their nuclei. The chemical properties of such similar atoms are exactly alike, and the two kinds of atoms appear to be the same element. Since, however, there is a difference in their atomic weights, they are not in reality identical. There are, for example, two kinds of chlorine atoms with different atomic weights, and more than one kind of lead atoms. The word *isotopes* is used to describe atoms which have the same atomic number but different atomic weights.

128. Many Elements Act Both as Metals and as Non-metals. — Carbon, atomic number 6 (Fig. 57), has four electrons in its outer ring. This is just half the number needed. We might expect that carbon would show both + and − valence. This is a fact, for the element combines both with metals and with non-metals. Nitrogen (Fig. 57), atomic number 7, has five electrons in the outer ring. Thus it might either lend five electrons, as it evidently does in the compound N_2O_5, or borrow three, as it does in NH_3. Almost any element can show this double tendency. Sulphur, while it usually has a valence of − 2, sometimes has one of + 6. An element is said to show *amphoteric* properties in such cases. In addition many elements show two or more different valences; iron sometimes has a valence of + 2, sometimes + 3. The explanation is not known at present in all cases.



Nitrogen Atom Carbon Atom

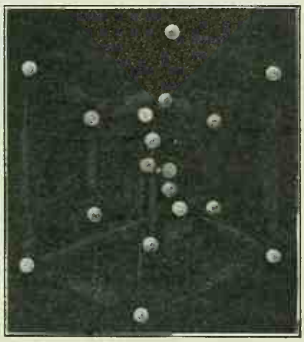
FIGURE 57.

Two elements which act either as lenders or as borrowers according to circumstances. Why?

Some elements, like helium, neon, and argon, do not enter into combination with any other elements. These elements may be considered as having a valence of 0, and each has its outer ring of electrons complete (Fig. 58).

129. Valence is a Great Aid in Writing Formulas. — Suppose we wish to write the formula of calcium chloride. The valence of calcium is + 2, that of chlorine −1. Evidently one calcium atom can supply two different chlorine atoms

with the one electron each needs. Thus the formula would probably be $CaCl_2$. Analyses confirm this conclusion. Aluminum has a valence of + 3, oxygen − 2. Hence one aluminum atom has too many electrons for one oxygen atom, but not enough for two oxygen atoms. Therefore two aluminum atoms, having a total of six electrons, can meet the needs of three oxygen atoms which together require this number of electrons. The formula we expect is Al_2O_3. Experiments confirm this.



Argon Atom

FIGURE 58.

An element which is completely without chemical properties because its 18 electrons are exactly enough to complete three rings. This arrangement shows them in three dimensions, as if they were motionless.

The general rule for writing the formula of a compound consisting of two elements is this: if the positive atom has the same valence as the negative, one atom of each element is needed; if the two valences are different, the total number of electrons borrowed and lent is the least common multiple of the two valences. Examples: The formula of zinc sulphide is ZnS, because the valence of zinc is + 2, and that of sulphur is −2. The formula of silicon oxide is SiO_2, because the valence of silicon is + 4 and that of oxygen is − 2. The least common multiple is 4. Hence one atom of silicon needs two of oxygen. The formula of ferric oxide is Fe_2O_3, because the valence of ferric iron is + 3, that of oxygen is − 2, and the least common multiple is 6. Two atoms of the iron have a total lending capacity of six electrons, and three oxygen atoms need to borrow six electrons.

130. Valences of Important Elements. — If one knows the atomic number of an element, he can easily determine the valence. But it is highly profitable to memorize certain important valences.

TABLE OF VALENCES

VALENCE OF +1	+2	+3	+4
Hydrogen H	Barium Ba	Aluminum Al	Carbon C
Mercury (ous) Hg	Calcium Ca	Iron (ferric) Fe	Silicon Si
Potassium K	Copper (ic) Cu		
Silver Ag	Iron (ferrous) Fe		
Sodium Na	Lead Pb		
	Magnesium Mg		
	Mercury (ic) Hg		
	Zinc Zn		
VALENCE OF −1	**−2**	**−3**	**−4**
Bromine Br	Oxygen O	Nitrogen N	Carbon C
Chlorine Cl	Sulphur S		
Iodine I			

The formulas obtained by the rules given above are, in most cases, the ones discovered on analysis of the compound. The final decision in the matter, of course, depends on analysis, not on theory.

131. Some Groups of Atoms Act like Single Atoms. — After chemists began to get formulas by analysis, it was soon discovered that definite groupings of certain elements appeared repeatedly in different compounds. For example, many compounds are found which always contain one hydrogen atom for each oxygen atom that is combined with

a third element. This fact is shown in such formulas as NaOH, KOH, $Ca(OH)_2$, $Al(OH)_3$. The OH group is called the *hydroxyl* radical. Four oxygen atoms are also found frequently in association with one sulphur atom, as shown by the formulas Na_2SO_4, $CaSO_4$, and $FeSO_4$. These groups generally cling together in going from combination with one element to combination with another. This gave rise to the idea of *radicals*. The word means a group of atoms which act like a single atom. The SO_4 group is called the *sulphate* radical.

132. Radicals Have Valences. — The radical SO_4 has a valence of -2. This happens because the four oxygen atoms, needing a total of eight electrons, are only partly satisfied by the six already borrowed from the one sulphur atom. Two more are still needed. So the radical as a whole is a *borrower* of two electrons. Another radical, called ammonium, NH_4, has a valence of $+1$ because the nitrogen atom, with its five free outer electrons, having lent only four to the four hydrogen atoms (which can act as borrowers as well as lenders), has one still available to supply the need of some negative element or radical.

Formulas containing radicals can be written by the same rules used for simple compounds. Parentheses are used to include the group, with the subscript number, if one is needed, written outside, to indicate how many of the radicals are present in the formula. This method makes it possible for the eye to recognize readily the presence of the radical. Examples: $(NH_4)_2S$, ammonium sulphide, containing the ammonium radical; $Fe_2(SO_4)_3$, ferric sulphate, containing the sulphate radical; and $Al(OH)_3$, aluminum hydroxide, containing the hydroxyl radical.

133. Important Radicals. — The following table gives the valence of some important radicals.

Valence of +1	−1	−2	−3
Ammonium NH_4	Hydroxide OH Nitrate NO_3 Bicarbonate HCO_3	Sulphate SO_4 Carbonate CO_3 Sulphite SO_3	Phosphate PO_4

134. Naming Chemical Compounds. — The pupil has probably already observed that a very simple rule is followed in naming a compound which contains only two elements. The positive element is used first, with its name unchanged, followed by the name of the negative element with its last syllable changed to **-ide**. Examples: NaCl, sodium chlor**ide**; Al_2O_3, aluminum **oxide**. Sometimes a prefix is added to the name of the negative element to indicate the number of its atoms in the molecule. Examples: H_2O_2, hydrogen **dioxide**; MnO_2, manganese **dioxide**; SO_3, sulphur **trioxide**; P_2O_5, phosphorus **pentoxide**.

A positive element not infrequently has two different valences. In these cases a suffix is added to the name of the positive element to indicate which valence is exhibited in the particular compound; **-ous** indicates low valence, **-ic** high valence of the positive element. Examples: $FeCl_2$, ferr**ous** chloride; $FeCl_3$, ferr**ic** chloride; HgCl, mercur**ous** chloride; $HgCl_2$, mercur**ic** chloride.

When radicals are present in a compound, its name includes the name of the radical used unchanged. Examples: $Zn(NO_3)_2$, zinc nitrate; $Al_2(SO_4)_3$, aluminum sulphate; $(NH_4)_3PO_4$, ammonium phosphate; Na_2SO_3, sodium sulphite.

In the name of an acid **-ous** indicates less oxygen and **-ic**

more oxygen. Thus we have sulphurous acid, H_2SO_3, which may also be called hydrogen sulphite, and sulphuric acid, H_2SO_4, hydrogen sulphate. The salts formed from the **-ous** acids have the ending **-ite**; those formed from **-ic** acids end in **-ate**. The formula of sodium sulphite is Na_2SO_3; that of sodium sulphate is Na_2SO_4.

SOME ACIDS AND THEIR SALTS

NAME OF ACID	FORMULA	SALTS FORMED	ILLUSTRATIONS OF SALTS
1. Hydrochloric acid	HCl	Chlorides	NaCl, sodium chloride
2. Hypochlorous acid	HClO	Hypochlorites	NaClO, sodium hypochlorite
3. Chloric acid	$HClO_3$	Chlorates	$KClO_3$, potassium chlorate
4. Hydrosulphuric acid	H_2S	Sulphides	ZnS, zinc sulphide
5. Sulphurous acid	H_2SO_3	Sulphites	K_2SO_3, potassium sulphite
6. Sulphuric acid	H_2SO_4	Sulphates	$CuSO_4$, copper sulphate
7. Nitrous acid	HNO_2	Nitrites	$NaNO_2$, sodium nitrite
8. Nitric acid	HNO_3	Nitrates	$Pb(NO_3)_2$, lead nitrate
9. Phosphoric acid	H_3PO_4	Phosphates	$FePO_4$, iron phosphate
10. Acetic acid	$H(C_2H_3O_2)$	Acetates	$Pb(C_2H_3O_2)_2$, lead acetate
11. Carbonic acid	H_2CO_3	Carbonates	$CaCO_3$, calcium carbonate
12. Hydrobromic acid	HBr	Bromides	AgBr, silver bromide
13. Hydriodic acid	HI	Iodides	KI, potassium iodide
14. Hydrofluoric acid	HF	Fluorides	CaF_2, calcium fluoride

SUMMARY

Atoms are made up of two parts, a nucleus and outside electrons. **The nucleus** consists of positive particles of electricity, called **protons**, and a nearly equal number of negative particles called **electrons.** There are always more protons than electrons present in the nucleus.

The outside electrons are always equal in number to the excess protons in the nucleus, and are at relatively considerable distances from it.

The outside electrons tend to arrange themselves **in rings**, two in the first, eight in the second and in the third, and eighteen in each of the successive rings.

The atomic number of an element is the total number of its out-

side electrons. We can tell what the valence and other chemical properties of the element are by knowing its atomic number.

An element is completely inactive chemically when the number of outside electrons is exactly right to form complete rings.

An element is active chemically, more or less, when the number of outside electrons is not enough to form complete rings.

When the number of electrons in the outside ring of an atom is less than half the number required for the outside ring, **the element is a metal.** The smaller the number of electrons, the more active the metal. When the number in the outside ring is more than half, **the element is a non-metal,** and if the number is nearly the required one, the element is very active. There can be either positive valence or negative valence. Metals have positive valence. Non-metals have negative valence.

The valence can be determined by calculating the number of electrons that are left to form the outside ring. If the number is less than half that needed for this ring the valence is equal to the number of electrons, and is positive. If the remaining number of electrons is more than half, the valence is negative and is equal to the number of additional electrons needed to make a complete ring.

Many elements show **two valences.** Sometimes one valence is positive, the other negative. This is especially noticeable in elements whose outside ring contains about half the necessary 8.

Chemical action results from the tendency of metals or positive elements to lend their loosely held electrons to fill up rings of negative elements.

The number of atoms needed for chemical combination can be found from the valences of the two elements. As many atoms of each will be needed as will give a total of electrons equal to the least common multiple of the two valences concerned.

Radicals are groups of two or more atoms which go about in chemical action, keeping their identity. Radicals act some-

what as if they were single atoms. Radicals appear frequently in chemical formulas.

The valence of a radical is the net number of electrons which the group of elements can either lend or borrow; radicals, like elements, can have either positive or negative valence. The rule for writing formulas involving radicals is the same as that for writing simple formulas.

A compound formed from two elements is named by retaining the name of the positive element, followed by the name of the negative element with its last syllable modified to **-ide.**

A compound containing a radical or radicals is named by using the name of the radical unchanged. An exception is found in the naming of the metallic hydroxides. These contain the hydroxyl radical, OH.

Acids with names **ending in -ous** have **salts** with names **ending in -ite. Acids** with names **ending in -ic** have **salts** with names **ending in -ate.**

EXERCISES

1. Give the names of scientists whose work helped to establish the electron theory of the atom, and tell the principal contribution of each.

2. What reasons are there for believing that all atoms are made up of electricity?

3. What is the *atomic number* of an element? What experiments are necessary to determine the atomic number?

4. What are the names of the two parts of an atom? Of what does each part consist? Which part plays the greater rôle in determining the chemical properties of the element?

5. Make a diagram to indicate the constitution of the element whose atomic number is 4; whose atomic number is 5; whose atomic number is 10.

6. Make a table like the following and fill in the blanks.

Atomic Number	Number of Electrons	Number of Electrons in Outer Ring	Active or Inert	Metal, Non-metal, or Amphoteric	Valence (+ or − and Number)	Name of Element (see p. 120)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

7. Define *valence*. Of what use is it to know the valence of an element?

8. Make a table like that on the opposite page and fill in the blanks with the formulas of the compounds indicated.

	Bromides Br^-	Chlorides Cl^-	Iodides I^-	Hydroxides OH^-	Nitrates NO_3^-	Bicarbonates HCO_3^-	Sulphates SO_4^{--}	Oxides O^{--}	Sulphides S^{--}	Carbonates CO_3^{--}	Phosphates PO_4^{---}
Sodium, Na^+											
Potassium, K^+											
Silver, Ag^+				×							
Ammonium, NH_4^+								×			
Mercury, Hg^+ (mercurous)				×							
Mercury, Hg^{++} (mercuric)										×	
Copper, Cu^{++}			×							×	
Calcium, Ca^{++}											
Barium, Ba^{++}											
Lead, Pb^{++}											
Magnesium, Mg^{++}											
Zinc, Zn^{++}											
Iron, Fe^{++} (ferrous)											
Iron, Fe^{+++} (ferric)			×			×				×	
Aluminum, Al^{+++}						×				×	

9. What is meant by the term *radical?*

10. How can the valence of a radical be calculated?

11. Name the chemical compounds formed by the following chemical unions: sodium and bromine; potassium and oxygen; magnesium and chlorine; calcium and sulphur; carbon and chlorine; calcium and carbon; aluminum and sulphate group; potassium and a nitrate group; chlorine and an ammonium group; calcium and a phosphate group.

12. What things are determined by the free electrons of an atom? By the nucleus?

13. Give an example of *isotopes.* What does the term indicate?

14. Explain why electric currents flow better through aluminum than through sulphur.

15. Why do we speak of atoms of metals as *lenders?* Of atoms of non-metals as *borrowers?*

16. Why are two atoms of hydrogen needed for combination with one atom of oxygen? Why four of chlorine for one of carbon?

17. Is hydrogen a metal or a non-metal? Explain.

CHAPTER XII

SODIUM AND POTASSIUM

135. Preparation of Sodium and Potassium. — The great chemical activity of these elements and the stability of their compounds made the separation of sodium and potassium a difficult chemical problem. Like many others, it was solved by the application of electricity. Sir Humphry Davy, in 1807, obtained both sodium and potassium by the electrolysis of their melted hydroxides.

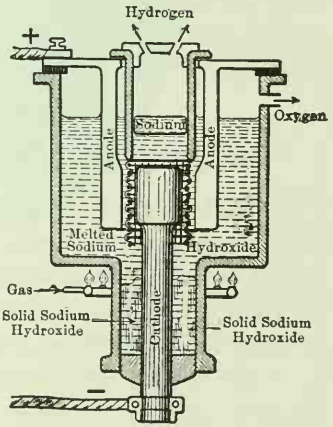


FIGURE 59.

Because sodium is a very active element, it requires much energy to separate it from its compounds. The electric current is passed through melted sodium hydroxide, decomposing it into sodium, hydrogen, and oxygen.

In making sodium commercially the sodium hydroxide is contained in an iron pot (Fig. 59), in which it is melted. The cathode is an iron rod coming up through the bottom of the cylinder, from which it is insulated by a layer of solid sodium hydroxide. The anode is an iron or nickel cylinder coming down from the top and surrounding the cathode. A metal cylinder with removable cover is suspended so as to come down inside the anode cylinder.

When the current is passed through the melted hydroxide, the sodium and hydrogen appear at the cathode and the oxygen at the anode. Suspended from the metal cylinder is a cylinder of wire gauze through which the fused hydroxide can pass, but which prevents the passage of bubbles of the gas or globules of melted sodium. The molten sodium, being lighter than the melted sodium hydroxide, rises to the surface above the cathode, and is ladled off from time to time. The hydrogen escapes through holes in the cover and the oxygen is led off through a pipe from the side. The heat generated by the passage of the current keeps the upper layer of the hydroxide melted. The equation for the electrolysis is:

$$2\,NaOH \longrightarrow 2\,Na + O_2 + H_2$$

Potassium can be prepared by the same process.

136. Physical Properties of Sodium. — The essential physical property of metals is their ability to conduct heat and electricity. In addition they are usually *malleable*, that is, they can be hammered, rolled, or pressed into shape. A metal also usually has a peculiar shine, known as a *metallic luster*, which differs from the glitter of polished nonmetallic surfaces because the metal is opaque. At first sight a beginner is apt to think that sodium is not a metal because it differs from the common metals such as iron or copper in being soft enough to cut with a knife, light enough to float on water, and so malleable that it can be shaped by slight pressure. It has, however, the essential metallic characteristics, such as the ability to conduct heat and electricity, and is a metal in the physical as well as in the chemical sense. We should expect these properties from the fact that the sodium atom has only one electron in its outer ring.

Sir Humphry Davy (1778–1829) was the most brilliant of English investigators. He early appreciated the value of the atomic theory and adopted it. He discovered the anesthetic properties of nitrous oxide. He made a very extended study of the effect of passing an electric current through substances and solutions, discovering by this means several new elements, notably sodium and potassium.

Davy explained the chemical nature of acids as compounds of hydrogen, a view not hitherto held. He announced chlorine as an element. He is famed as the inventor of the miner's safety lamp.

For seven years he was president of the Royal Society of England.

137. Chemical Activity. — Sodium is a very active element chemically. It burns readily in oxygen and in chlorine, and is an energetic reducing agent. The color of its flame is bright yellow, and this color is imparted to a non-luminous flame when any sodium compound is heated in it.

138. Action with Water. — The most striking chemical property of sodium is its action with water. Exposed to moist air, it tarnishes almost instantly on account of the formation of a layer of sodium hydroxide. In perfectly dry air, it remains unchanged at ordinary temperatures. When thrown on water, it skims over the surface with a hissing sound (§ 31). The water is rapidly decomposed, one half the hydrogen being set free, and the sodium combines with the oxygen and the other half of the hydrogen to form sodium hydroxide:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

The sodium hydroxide dissolves in water and the solid hydroxide may be obtained by evaporation. A large amount of energy is liberated in the decomposition of water by sodium. This may be readily shown by dropping a bit of sodium on a moist piece of filter paper. In this way the heat is liberated at one place and is sufficient to ignite the hydrogen. On account of its ready action with water, sodium is always kept under kerosene or some other oil containing no oxygen. Commercially it is sold dry in air-tight containers.

139. Uses of Sodium. — This metal is used for making sodium peroxide, sodium cyanide, and many complex compounds used as dyes and drugs. Its chemical activity makes

it valuable for the laboratory study of typical chemical reactions.

140. Properties of Potassium. — Potassium is a silvery white metal with a slight bluish tinge. It is softer than sodium, lighter, and melts at a lower temperature. Although sodium and potassium are solids at ordinary temperatures, it is possible to prepare an alloy of the two which is a liquid.

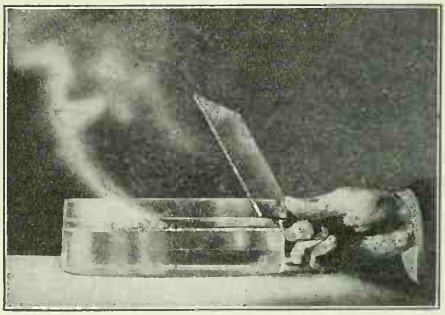


FIGURE 60.

When potassium touches water a violent reaction results. So much heat is produced that the hydrogen liberated in the action is set on fire.

The chemical properties of potassium closely resemble those of sodium, but potassium is more active. It decomposes water, forming potassium hydroxide and liberating hydrogen. The energy produced is sufficient to ignite the hydrogen (Fig. 60). Potassium and its compounds impart a violet color to the flame. As the presence of a slight trace of sodium obscures the potassium flame, several thicknesses of cobalt blue glass should be interposed between the flame and the eye in order to absorb the yellow light produced by the sodium.

141. Bases. — A solution of sodium hydroxide turns red litmus blue, an action exactly the reverse of that of an acid. Substances behaving like sodium hydroxide in this respect are said to have an *alkaline* or *basic reaction*.

When we mix solutions in which the weights of hydro-

chloric acid and sodium hydroxide are proportional to their molecular weights, there is a rise of temperature, and the resulting solution affects neither red nor blue litmus. This solution contains sodium chloride, a fact that is indicated by its taste. As the hydrochloric acid and the sodium hydroxide have both lost their characteristic properties, the resulting solution is said to be *neutral* and the process is known as *neutralization*. The change may be expressed by the equation:

$$HCl + NaOH \longrightarrow H_2O + NaCl$$

There are many substances which, like sodium hydroxide, act in this way with acids. They are called *bases*.

A base is the hydroxide of a metal or of a metallic radical.

Water solutions of bases give alkaline reactions. Potassium hydroxide, calcium hydroxide, and ammonium hydroxide are other common soluble bases. Bases may or may not be soluble in water. Copper hydroxide is an illustration of a base that is insoluble in water. Insoluble bases do not give an alkaline reaction.

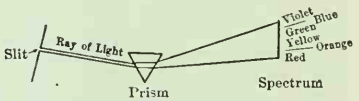


FIGURE 61.

All light is bent in going through a prism; violet is bent most and red least. A beam of sunlight is thus formed into a band of rainbow colors, and light from flames colored by the presence of certain elements is separated into characteristic components as shown in the illustration opposite page 144.

142. Spectrum Analysis. — The colors imparted to flames by different elements furnish a simple and valuable method of analysis. The different colors found in light are bent to different degrees in passing through a prism, and are thus separated from each other (Fig. 61). The band of light thus produced is known as a *spectrum*, and the instrument used to produce

and to view the spectrum is called a *spectroscope* (Fig. 62). It was invented by Bunsen and Kirchhoff. The light to be studied is admitted through a narrow slit in the end of a tube, in such a way that it will fall in a parallel beam on a prism, the edges of which are parallel to the slit. When the beam emerges from the prism, the different colors are separated and the spectrum is viewed through lenses placed in another tube.

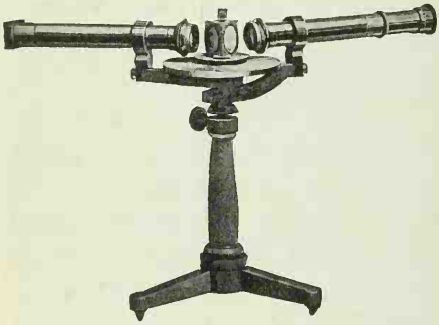
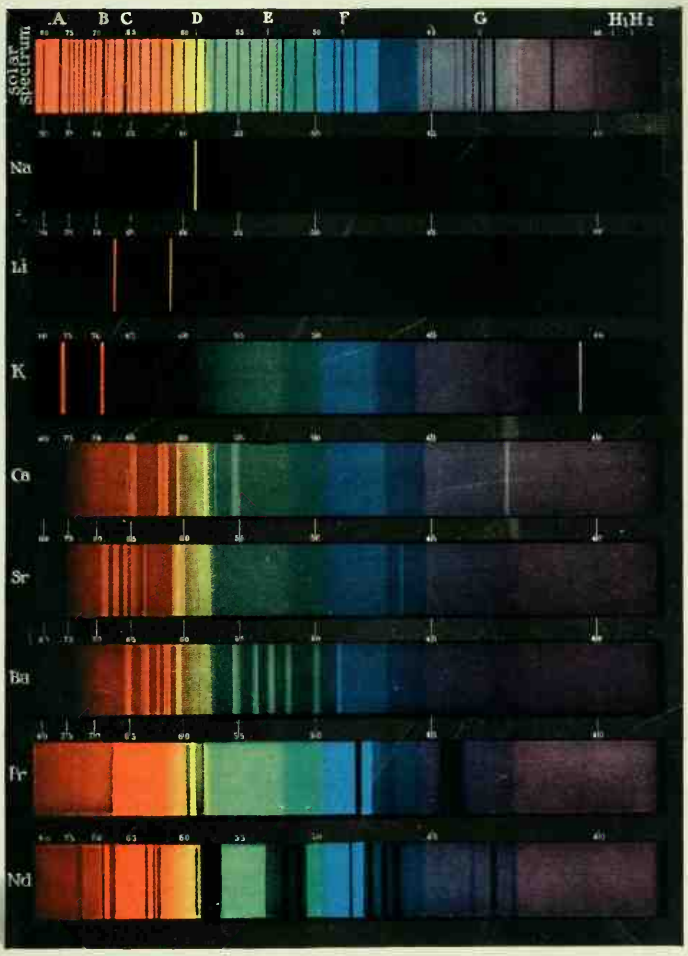


FIGURE 62.

A chemist can tell much about the composition of a substance by the color of light that it produces. This spectroscope is provided with a prism to separate colors into a spectrum, and with telescopes to direct the rays of light and magnify the spectrum.

White light, produced by an incandescent solid, gives a spectrum consisting of a continuous band of color, shading from red through orange, yellow, green, blue, and indigo to violet. When the light is due to incandescent vapors, the spectrum consists of a series of bright lines, the color and position of which differ for each element. The yellow color referred to above is due to the presence of sodium vapor in the flame. This may be produced most conveniently by placing in a flame a rod of common glass, which contains a sodium compound. Such a flame when viewed with a good spectroscope shows two yellow lines very close together. The spectrum of potassium consists of two lines in the red end of the spectrum and a line in the violet end.

Lithium is a rare metal with properties that are very



VARIOUS SPECTRA

At the top is the spectrum of the sun, crossed by Fraunhofer's lines. The other spectra are, reading downward, those of sodium, lithium, potassium, calcium, strontium, barium, praseodymium, and neodymium.

similar to those of sodium and potassium. It was thought to exist in very few minerals until the spectroscope showed that small quantities of it were widely distributed throughout nature. Its spectrum consists of a bright red line and a very faint yellow line. The presence of one millionth of a milligram of lithium can be shown by means of the spectroscope. In most cases the spectroscope affords us the most delicate and certain test we have for the presence of an element.

The observance of unfamiliar lines in the spectra of known elements has led in several instances to the discovery of elements hitherto unknown. By its spectrum, helium was known to exist in the sun before this element was found on the earth. The illustration facing page 144 shows the spectrum of the sun, and that of a number of elements. The last two elements are metals of the rare earths, præsodymium and neodymium, respectively.

143. A Family of Elements. — Because of the similarity of chemical and physical properties, the elements lithium, sodium, and potassium are thought of as members of a chemical family, and are called collectively the *alkali metals*. There are two additional members, both very rare, known as rubidium and caesium. Until the discovery of electrons, no explanation was known for the strong resemblances among all these elements. Now it is easily understood, for each of these metals has only one free electron in its outer ring. They are all lending elements, with one electron to furnish in an act of chemical combination. Note that physical as well as chemical properties are rendered very similar by the same number of electrons in the outer ring.

SUMMARY

Sodium and **potassium** are made by the electrolysis of their hydroxides or chlorides.

	Atomic Weight	Specific Gravity	Melting Point	Boiling Point
Sodium . . .	23.0	.97	97.6°	877°
Potassium . .	39.1	.87	62.5°	757°

Both **metals** are soft and light. They react with water to form hydroxides, and with acids to form salts.

Their **compounds** are characterized by the colors they impart to a non-luminous flame.

The **hydroxides** of sodium and potassium are typical bases. Their solutions turn litmus blue and neutralize acids.

A **base** is the hydroxide of a metal or a metallic radical.

Neutralization is the mixing of an acid and a base in such proportions that the water solution of the products affects neither red nor blue litmus.

Elements that resemble each other strongly are said to belong to a **chemical family.** Lithium, sodium, and potassium belong to the family of alkali metals.

EXERCISES

1. Why was the preparation of metallic sodium a difficult chemical problem to solve?

2. Does melted sodium hydroxide act on iron and nickel? Give a reason for your answer.

3. Why cannot a water solution of sodium hydroxide be used for the electrolytic preparation of sodium?

4. Sketch the apparatus for making sodium. Label each part. What are the uses of the wire gauze? What goes to the cathode? To the anode?

5. Compare the properties of sodium with the corresponding properties of metals with which you are more familiar, for example, iron, copper, silver. Do you find any resemblances?

6. Why is sodium classed as a metal?

7. What are the most essential properties of metals from the chemical point of view?

8. Why does neither sodium nor potassium occur in an uncombined state in nature?

9. How should sodium be stored? Explain.

10. What properties of sodium prevent its use as an electric conductor?

11. Calculate the quantity of sodium that could be obtained from 1 kilogram of pure sodium hydroxide.

12. Why would it be extremely dangerous to drop a large piece of sodium or potassium into water?

13. The atomic number of lithium is 3, that of sodium 11, of potassium 19. Make a diagram of each, showing the number in successive rings. What similarities do you note? Why are all these elements metals? Why is the valence 1 in each case?

14. Write the equation for the reaction of potassium with water. What would be obtained if the resulting solution were evaporated to dryness?

15. Calculate the quantity of sodium hydroxide that would be formed by the action of 5 grams of sodium on water. What weight of hydrogen would be evolved?

16. State two facts which show that potassium hydroxide should be classed as a base.

17. What is neutralization?

18. What weight of hydrogen chloride would be required for the complete neutralization of 2.63 grams of sodium hydroxide?

19. What right have we to believe that many of the terrestrial elements exist in the sun?

20. Mention two methods for preparing hydrogen from water.

21. What would be the danger if the hydrogen and oxygen produced in the electrolytic preparation of sodium were allowed to mix in the apparatus?

22. Why are lithium, sodium, and potassium thought of as being related to each other chemically?

23. What weight of potassium hydroxide would be formed by the reaction of 5 grams of potassium with water? What weight of hydrogen would be evolved?

CHAPTER XIII

SOLUTION[1]

We have found that many of the reactions studied take place only in the presence of water, even though the water itself does not react. It is one of the purposes of this chapter to explain this fact.

144. Conducting Power of Solutions. — Solutions differ from each other greatly in their power to conduct electricity. We have already seen that water solutions of sodium chloride and sulphuric acid (electrolysis of water) readily permit the passage of the current. We may test solutions for their ability to conduct electricity by arranging a circuit that includes a source of current, the substance to be tested, and some instrument to detect the passage of the current, as an incandescent lamp, connected in series. Figure 63 shows a beaker

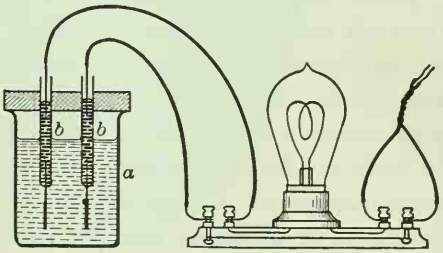


FIGURE 63.

By this apparatus we can determine whether or not the molecules of a given substance separate into ions when the substance is dissolved in water. The current passes through the solution only when ions are present.

[1] NOTE TO INSTRUCTOR. — Although this and the following chapter may be taken up at this point, many instructors prefer to postpone their discussion until the students have become acquainted with a wider range of chemical phenomena.

a containing the solution to be tested; *b*, *b* are electrodes with mercury contacts.

The incandescent lamp serves two purposes. Its resistance cuts down the current to a strength suitable for passing through a solution. Secondly, if the lamp lights, the current must be passing through the liquid in the circuit, and the solution is a conductor. The brilliancy with which the lamp glows indicates roughly how well the solution in the circuit conducts the electric current.

When distilled water is put into the circuit, the lamp does not even glow; hence, in those water solutions which are conductors, the current must be carried by the aid of the dissolved substance. A water solution of hydrochloric acid conducts the current readily; a solution of sugar fails to conduct; but a solution of sodium hydroxide, a typical base, proves as good a conductor as hydrochloric acid. Solutions of sulphuric acid, potassium hydroxide, sodium chloride, sodium sulphate, and copper sulphate, all allow the lamp to glow brilliantly. When a solution of acetic acid is tested, the lamp barely glows. In all of these cases a chemical action goes on while the current is passing and products are invariably formed at each electrode. Glycerine, alcohol, and many similar compounds are found to be non-conductors. They are not changed by the presence of electrodes in their solutions.

145. Electrolytes and Non-electrolytes. — Our circuit includes two different classes of conductors. The first consists of solid conductors, chiefly metallic, such as the copper wire and the filament of the lamp. These conductors undergo no permanent change in carrying the current. The other class includes those liquids that we have found to be

Michael Faraday (1791–1867), the son of a blacksmith, was born in a suburb of London. At the age of fourteen he was apprenticed to a bookbinder, but devoted his spare time to reading and attending lectures on physical science. He heard Davy lecture at the Royal Institution and wrote him, expressing a desire to enter the service of science. He became Davy's laboratory assistant in 1813. Faraday sacrificed much in order to devote his time to pure science, and his discoveries are numerous, including benzene, magneto-electric induction, electrochemical equivalents, and the liquefaction of several gases. He expressed the belief that gases are liquids having a very low boiling point.

conductors. They apparently have components which are free to move toward the electrodes. In these liquid conductors, the transmission of electricity is attended by the decomposition of the solute. A liquid that is permanently decomposed during the passage of an electric current is called an *electrolyte*. The name given to the process is *electrolysis*.

Arranging the electrolytes and non-electrolytes in two columns, we obtain results similar to those indicated in the table:

Electrolytes	Non-electrolytes
hydrochloric acid	distilled water
sulphuric acid	
sodium hydroxide	sugar
potassium hydroxide	
sodium chloride	glycerine
sodium sulphate	
copper sulphate	alcohol

An examination of the column of electrolytes shows that it contains only substances which are rather active chemically. The second column contains only those which are inactive. There seems to be some connection between electrical conductivity and chemical activity. The discovery of this relationship led to a more careful study of the properties of water solutions.

146. Effect of Dissolved Solids on the Freezing Point. — Under standard pressure pure water freezes at 0° C. and boils at 100° C. The addition of any soluble solid lowers the freezing point and raises the boiling point. We shall discuss only the freezing point. All water solutions freeze at a lower temperature than pure water. Careful measure-

ments show that the amount the freezing point is depressed depends on the mass of the substance added. A solution containing 10 grams of sugar to 1 liter of water will freeze at a point twice as far below 0° as one containing 5 grams of sugar to 1 liter of water. According to the atomic theory, 10 grams of sugar contain twice as many molecules as 5 grams. Therefore, the lowering of the freezing point of the pure solvent is proportional to the number of sugar molecules dissolved.

The depression of the freezing point of water (Fig. 64)[1] produced by equal numbers of molecules of different substances has been carefully determined. To get equal numbers of molecules, a gram-molecular weight (§ 115) of each substance was dissolved in 1 liter of water. Thus 46 grams of alcohol, C_2H_5OH, and 342 grams of sugar, $C_{12}H_{22}O_{11}$, were each dissolved in a liter of water. In both cases the resulting solutions froze at $-$ 1.86° C. It was further found that a solution of any non-electrolyte containing a gram-molecular weight of the solute to the liter gave this same lowering of the freezing point. If weights of non-electrolytes proportional to their molecular weights are dissolved in equal volumes of the same solvent, the solutions will freeze at the same temperature. This is strictly true for dilute solutions only. This indicates that the depression of the freezing point is dependent on the *number* of molecules present and not on the weight or kind of these molecules. But if common

[1] Figure 64 represents an apparatus for determining the depression of the freezing point. A Beckmann thermometer (*a*) is used and the liquid to be frozen is held in the inner tube (*b*). Through the side tube (*c*) is introduced the substance whose effect on the freezing point of the pure solvent is to be determined. A stirring rod (*d*) moves up and down in the solution, which is cooled by a freezing mixture contained in the outer vessel (*e*).

salt is used, we find that, in dilute solution, the freezing point is lowered nearly twice as much as in the case of a solution of a non-electrolyte containing the same number of molecules. This can be explained by assuming the presence of *twice as many particles* in a solution containing a gram-molecular weight of salt as in the same volume of a solution containing a gram-molecular weight of sugar. In other words, we have reason to think that when they are dissolved in water, all or nearly all of the salt molecules are separated each into two particles. All other electrolytes behave as salt does, while all non-electrolytes act like sugar.

In the case of electrolytes which dissociate into more than two particles, the lowering of the freezing point will be three or more times as great as in the non-electrolytes, according to the number of particles into which the molecule of the electrolyte dissociates.

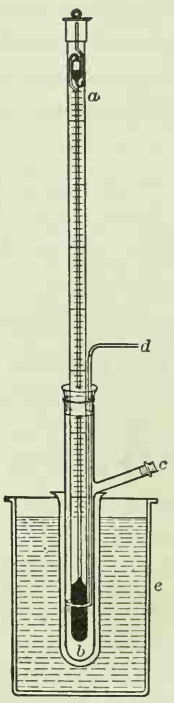


FIGURE 64.

This delicate thermometer shows that the lowering of the freezing point produced by solutes depends on the number rather than on the kind of particle. It shows that in all electrolytes part of the molecules are split into two or more ions.

147. Dissociation of Electrolytes. — A careful study of the boiling point shows a greater elevation in the case of electrolytes than in that of non-electrolytes, in proportion to the number of dissolved molecules. The differences produced by equal numbers of molecules of electrolytes and non-electrolytes, in the boiling point as in the lowering of the freezing point, may all be

explained by assuming that in electrolytes some of the dissolved molecules are broken up or *dissociated* into parts as soon as they are dissolved. In non-electrolytes, the molecules of the dissolved substance are not dissociated.

148. Ions. — To the moving particles that are formed in the electrolyte while solution is taking place, Faraday gave the name *ions,* meaning wanderers. A dilute hydrogen chloride solution is an electrolyte in which the depression of the freezing point is twice that produced by a non-electrolyte. This indicates that the hydrogen chloride molecules, *in the act of dissolving,* break up into two parts. These must correspond to the hydrogen and chlorine atoms. We know that they must be electrically charged, because they move in opposite directions *when the current is turned on* in a solution containing them. Since the hydrogen particles are attracted toward the cathode, or negative pole, these hydrogen particles must be positively charged. Similarly the chlorine particles must have negative charges, since they are drawn toward the positive pole or anode.

The following equation represents what takes place *when hydrogen chloride is dissolved in water:*

$$HCl \rightleftharpoons H^+ + Cl^-$$

It is a common error to suppose that the breaking up of a molecule into ions is produced by the electric current. As we have just shown, this dissociation takes place *in the act of dissolving.* Therefore, every solution of an electrolyte contains ions, and such a dissolved substance is said to be *ionized.*

An ion is an atom or a group of atoms carrying an electric charge.

149. Electric Charges on Ions. — The electron theory of the atom gives a simple explanation of the electric charges which the hydrogen ion and the chlorine ion carry, after molecules of hydrogen chloride have thus been *ionized* (or *dissociated*) on being dissolved in water. The chlorine part of the original molecule now wanders freely about the solution, carrying with it the one electron borrowed from the hydrogen atom. It is, of course, now negatively charged, for it has eighteen free electrons instead of the seventeen needed for electrical balance with the excess seventeen plus charges in its nucleus. The hydrogen atom is now charged positively, having lost for the time it is to remain in the solution, its one free electron. It is clear that neither the part we call hydrogen nor the part we call chlorine is a true atom; for both are now electrically charged. We call the one a hydrogen ion and write it H^+; the other a chlorine ion, written Cl^-.

150. Explanation of Electrolysis. — When the electrodes are dipped into a solution of an electrolyte, for example $CuCl_2$, the positively charged Cu^{++} ions are attracted to the negative electrode (cathode). There the positive charge of the Cu^{++} ion is neutralized by the negative electricity of the cathode, and the copper *atom* is deposited on this electrode.

Similarly, the negatively charged Cl^- ions move to the anode. The chlorine ions give up their electrons the instant they touch the anode, neutralizing in part the positive charge on that electrode. The particles of chlorine without their extra electrons are ordinary atoms, which unite in pairs to form molecules of chlorine gas, that bubbles off at the anode.

This process of the migration of the atoms continues as

long as the current passes, and as long as any electrolyte remains in the solution, for the current is maintained by ions which act as carriers of electricity. Furthermore, this explains why electrolytes are chemically changed during the passage of a current.

In giving the explanation of an electrolysis, it should be remembered that *the electric current is not the cause of the dissociation into charged particles, but simply determines the direction in which they move.* The dissociation took place while the substance was dissolving.

151. Differences between Ion and Atom. — Ions should not be confused with atoms. The existence of an electric charge on an atom entirely changes its properties, as may be seen from the electrolysis of sodium chloride. When sodium chloride is dissolved in water, although sodium ions are formed, they do not react with the water. But when a current is passed through the salt solution, the sodium ions lose their charge when they touch the cathode and become sodium atoms. These atoms react with water to form sodium hydroxide and hydrogen. The atoms of chlorine, liberated at the anode, tend to combine in pairs to form molecules of green chlorine gas; ions of chlorine are colorless and repel each other because they possess like charges.

The differences between ion and atom may now be stated as follows: first, they differ in chemical properties, for an ion has an electric charge because it has lost or gained electrons, while an atom has no electric charge; second, a single ion often includes several atoms of different elements.

152. Chemical Activity of Electrolytes. — Nearly all chemical actions require the presence of water. When

two solutions of electrolytes are mixed, action takes place rapidly if one of the products of the reaction is either insoluble or gaseous, so that it is removed from the field of action. In general, electrolytes are very active chemically because, instead of molecules, the solutions contain ions which can enter into a great variety of combinations. Non-electrolytes, on the other hand, usually show very little activity because only molecules are present in their solutions.

153. Conditions That Determine the Degree of Dissociation. — When an electrolyte dissolves, some of its molecules enter into solution without dissociating, while others separate into ions. The extent to which the electrolyte dissociates depends on several conditions. The most important is the volume of the solvent. All of the particles in the solution, whether molecules or ions, are in constant motion, and in frequent collision with each other. The splitting of molecules into ions, and the reverse action of the combining of ions into molecules, are occurring all the time. When there is a large volume of solvent, there is room for a greater number of particles; the collisions are, therefore, less frequent, and consequently a large proportion of the substance is in the ionized state. Hence, in a dilute solution a greater proportion of the molecules are dissociated than in a concentrated solution. Experiments confirm this conclusion.

Experiments also indicate that there is a greater degree of dissociation at a high than at a low temperature.

154. Degree of Dissociation Is Measured by Electrical Conductivity. — It will be readily seen that the more ions there are present in a given solution, the better it will conduct the current, for the ions act as carriers of electricity.

So we can compare the degree of ionization of electrolytes by comparing the conducting power of the solution, provided in every case there are corresponding weights of solute between the electrodes. Conductivity under these conditions is called *molecular conductivity.* We find, as we continue to dilute an electrolyte, that the molecular conductivity increases up to a certain point, beyond which it does not change. This might be expected, for at a certain dilution all the molecules are dissociated, and a further dilution causes no further dissociation. The effect of dilution on ionization is shown in the following table, in which m is the number of gram molecules in 1000 grams of water. The numbers give the relative conductivity.

m	HNO_3	HCl	KCl	NaCl
1.00	2770	2780	919	695
0.50	2991	3017	958	757
0.10	3225	3244	1047	865
0.05	3289	3330	1083	897
0.01	3395	3416	1147	962

155. Ionization of Acids and Bases. — Experiments show that the following substances, on entering into solution, ionize as shown by these equations:

$$HCl \rightleftarrows H^+ + Cl^-$$
$$HNO_3 \rightleftarrows H^+ + NO_3^-$$
$$H_2SO_4 \rightleftarrows 2\,H^+ + SO_4^{--}$$

(Note that the 2 before the H^+ means 2 separate ions of hydrogen, each of which has one positive charge.) We observe that all these substances produce hydrogen ions. These compounds have the characteristic properties of acids in a marked degree and are our common acids. Further-

Svante August Arrhenius was born at Wijk, Sweden, in 1859. He is the present director of the Physico-chemical Department of the Nobel Institute. His great work was the invention in 1887 of the modern theory of dissociation in electrolytes, commonly known as the ionization hypothesis. This conception has done much to bind into an orderly system many previously unexplained experimental observations.

Jacobus Henricus van't Hoff (1852–1911) was born at Rotterdam, Holland. He became Professor of Physical Chemistry to the University of Berlin in 1894. He possessed great depth of scientific imagination and will be remembered for his brilliant work in developing several of the generalizations of modern physical chemistry and for the application of physical chemistry to geology.

more, *all the substances* that we know as acids produce H^+ ions when they enter solution. We conclude, therefore, that the characteristic properties of acids are in reality the properties of hydrogen ions. It is the hydrogen ion, which is always positively charged, that is responsible for the sour taste of acids and for their power to turn litmus red. The presence of hydrogen in a compound does not make it an acid; the compound must give hydrogen ions in water solution. Liquefied hydrogen chloride, free from water, fails to act as an acid, because none of its molecules break up so as to give hydrogen ions.

An acid is a hydrogen compound whose water solution contains hydrogen ions.

Our strong bases ionize as follows:

$$NaOH \rightleftarrows Na^+ + OH^-$$
$$KOH \rightleftarrows K^+ + OH^-$$

All bases produce hydroxyl ions when they are dissolved. We conclude, therefore, that the characteristic properties of bases are, in reality, the properties of the hydroxyl ion. It is the hydroxyl ion which makes bases turn litmus blue, neutralize acids, and react with fats and oils. Most metallic hydroxides are extremely weak bases because they do not dissolve appreciably in water, and hence cannot produce many hydroxyl ions.

A base is a hydroxide of a metal or a metallic radical whose water solution contains hydroxyl ions.

156. Activity of Acids and Bases. — The chemical activity of an acid depends upon the extent to which its dissolved molecules are dissociated into ions. Hydrochloric acid is almost wholly dissociated into its ions in dilute solution. This is why it acts vigorously on metals and

neutralizes bases. Such an acid is spoken of as a *strong acid.* Nitric acid is another example of a strong acid. Sulphuric acid, which is dissociated only two thirds as much as the acids just mentioned, is not so strong an acid. Acetic acid is the type of a weak acid, because it is so slightly dissociated (less than 2% in dilute solution) that it does not act vigorously on most metals, and its reactions with other substances are slow.

The term *strong acid* must not be confused with the term *concentrated acid.* Concentrated sulphuric acid usually contains about 95% H_2SO_4, while concentrated hydrochloric acid contains but 37% HCl. Sulphuric acid, then, is usually the more concentrated, but it is the weaker acid of the two. Hydrochloric acid is the more reactive, since it is dissociated to a greater extent in water solution. In the preparation of hydrogen chloride, the reason for the displacement of hydrochloric acid by sulphuric acid is not that sulphuric acid is a stronger acid, but that it has a higher boiling point.

As in the case of acids, the strength of a base depends upon the degree of ionization it undergoes in solution. Sodium hydroxide and potassium hydroxide are almost completely dissociated in dilute solutions. They are types of strong bases.

157. Explanation of Neutralization. — When we mix dilute solutions of hydrochloric acid and sodium hydroxide, we have present in the mixture positive ions of hydrogen and sodium, and negative ions of chlorine and hydroxyl. Each positive hydrogen ion will attract a negative hydroxyl ion, and *vice versa.* The two ions combine, the equal opposite charges neutralize each other, and a molecule of undissociated water results. Indicating the sign of the charge by

+ or − above and to the right of the symbol, we may express this change by the equation:

$$H^+ + OH^- \longrightarrow H_2O$$

As water is practically undissociated (only two molecules in a billion), we may consider it as completely removed from the action as if it had formed an insoluble compound or precipitate. In the neutralization, for each H^+ ion withdrawn in this way a Cl^- ion is left, and for each OH^- ion a Na^+ ion remains. These will not unite permanently so long as water is present, for the sodium chloride is dissociated as fast as it is formed. The neutralization is complete, when there are neither H^+ nor OH^- ions left to give an acid or a basic reaction, and the solution then contains equal numbers of Na^+ and Cl^- ions. The equation showing these facts is:

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow H_2O + Na^+ + Cl^-$$

If the solution is now concentrated, the degree of dissociation is lessened, and Na^+ and Cl^- ions will unite to form undissociated sodium chloride. When evaporation is complete, we find that the sodium ions and the chlorine ions have completely united, forming crystals of salt.

158. Products of Neutralization. — We get similar results from the use of other acids and bases. Potassium hydroxide and hydrochloric acid give undissociated *water*, K^+ ions, and Cl^- ions. Nitric acid and sodium hydroxide yield undissociated water, Na^+ ions, and NO_3^- ions.

$$K^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + K^+ + Cl^-$$
$$Na^+ + OH^- + H^+ + NO_3^- \longrightarrow H_2O + Na^+ + NO_3^-$$

In every case of neutralization the products are:

(1) undissociated water;
(2) a solution containing positive ions from the base and negative ions from the acid;
(3) energy in the form of heat.

During the evaporation of the solvent the positive ions from the base unite with the negative ions from the acid to form a compound known as a *salt*.

159. Heat of Neutralization. — Neutralization, as a chemical process, is essentially the formation of undissociated water molecules. It is always accompanied by the liberation of heat. When dilute solutions of different strong bases, each containing the same number of gram-molecular weights per liter, are neutralized by a dilute solution of a strong acid, equal quantities of heat result from the neutralization of the acid with each base. This heat is known as the *heat of neutralization*.

The following table shows the heat of neutralization expressed in calories, using gram-molecular weights:

	HCl	HNO_3
NaOH	13,700 cal.	13,700 cal.
KOH	13,700 cal.	13,700 cal.

This uniformity in the heats of neutralization indicates that the reaction is the same in all these cases. The only common product is water.

The heat of neutralization, therefore, is the heat evolved by the formation of water from hydrogen and hydroxyl ions.

160. Charges Carried by Ions. — We have seen that one molecule of hydrochloric acid neutralizes one molecule of

sodium hydroxide, producing one molecule of water. But we find that to neutralize one molecule of barium hydroxide, $Ba(OH)_2$, two molecules of hydrochloric acid are required, according to the equation:

$$Ba^{++} + 2\,OH^- + 2\,H^+ + 2\,Cl^- \longrightarrow 2\,H_2O + Ba^{++} + 2\,Cl^-$$

The barium chloride is largely dissociated into barium ions and chlorine ions. In any solution, the positive charges must equal the negative charges. Therefore, in this case each barium ion must contain two positive charges to balance the negative charges on the two chlorine ions. *In electrolytes, the valence of each ion is numerically equal to the number of charges carried by it.*

161. Ionization in Other than Water Solution. — While ionization takes place to a higher degree in water than in other solvents, it seems certain that the separation takes place to at least a small extent in every case of solution.

Fused salts, even in the complete absence of water, often conduct an electric current. This indicates ionization.

With the careful study that has followed the development of the hypothesis of ionization, chemists have come to believe that in most cases chemical action takes place between ions rather than between molecules. With the aid of this theory many things not previously understood have been fully explained.

SUMMARY

Solutions are classified as **electrolytes** and **non-electrolytes**, according to their power to conduct electricity. The electrolytes include solutions of acids, bases, and salts.

The **effects of dissolved substances** on the boiling point and freezing point indicate that the molecules of the solute are dis-

sociated in the case of electrolytes. Electrolytes are more active chemically than non-electrolytes because of the separation of electrolytes into ions.

The particles into which a molecule dissociates are two or more kinds of **ion**, some positively charged, others negatively. The total of + charges is equal to the total of − charges. The charges result because borrowed electrons are retained in the act of dissociation. When an electric current is passed through an electrolyte, each ion passes to the electrode of opposite sign and is there discharged and liberated. **Acids** furnish **hydrogen ions** in solution; **bases** furnish **hydroxyl ions**, and **salts** furnish **metal and acid radical ions.** The percentage of ionization increases with the dilution until ionization is practically complete.

The **strong** or **active acids and bases** are those which are highly dissociated. The essential action in **neutralization** is the union of the **hydrogen** and the **hydroxyl** ions to **form undissociated water**; during evaporation, the union of the other ions to form a salt is completed. The strong acids and bases unite yielding the same heat of neutralization for equivalent quantities.

Hydrogen and metallic ions carry positive charges; the non-metallic ions, negative charges. The **valence** of an ion is numerically equal to the number of charges carried by it.

EXERCISES

1. How do you determine whether or not a given solution is an electrolyte?

2. When a beaker of acetic acid is put in circuit with an incandescent lamp, the lamp glows feebly, while the solution of sodium acetate allows it to glow brightly. What does this show?

3. Compare the freezing point of sea water with that of ordinary rain water.

4. Why will substances often react with each other in solution while they will not react in a dry state?

5. What ions are present in solutions of the following: KCl, $ZnSO_4$, $KClO_3$, NaOH?

6. Distinguish carefully between an ion of potassium and an atom of potassium. What causes the difference?

7. What element is common to all acids? What group of elements is common to all bases? Select an acid and a base and by an equation show that you understand the meaning of the term *neutralization*.

8. Show two essential differences between a solution of salt in water and the suspension of an insoluble powder in water.

9. Why does one gram molecule of hydrogen chloride produce the same lowering of the freezing point of water that two gram molecules of glycerine produce, when each is dissolved to form equal volumes of dilute solution?

10. Why is nitric acid a more active acid than sulphuric acid?

11. Give the changes that take place and the products formed in the following cases:

(*a*) when nitric acid is added to water;
(*b*) when a piece of caustic potash is dissolved in water;
(*c*) when the two solutions are mixed.

12. A piece of red litmus turns blue in a solution of sodium carbonate (Na_2CO_3). Name the ions shown to be present by this test.

13. State and explain, on the basis of the theory of electrolytic dissociation, what happens when a current of electricity is passed through a solution of sodium chloride.

14. Write equations, indicating ions, for the neutralization of potassium hydroxide with sulphuric acid; of nitric acid with ammonium hydroxide.

15. How is it known that metallic ions are positively charged? Non-metallic ions negatively charged?

CHAPTER XIV

WHY CHEMICAL ACTIONS GO TO AN END

162. Energy in Relation to Chemical Stability. — All through nature, those actions occur most readily which result in the liberation of energy. Thus a stone at the top of a hill possesses *potential* energy, and the stone rolls down hill spontaneously after being given a little start. As this happens the potential energy is changed into other forms, one of which is heat. The stone can be put back at the top of the hill only by supplying again the amount of energy which was lost during the descent. While energy is at hand in the heat of the air and other surrounding objects, nature makes no provision for a spontaneous absorption needed to put the stone back in its original position. So, *naturally*, the stone rolls down hill, not up.

We observe an analogous situation in chemical compounds. Some explode violently upon receiving a slight impulse, and liberate large amounts of energy. They are like the stone while it is at the top of the hill. Other compounds can be decomposed only by supplying a large amount of energy in the form of heat or electricity. These are like the stone which lies at the bottom of the hill.

Nitroglycerine, $C_3H_5(NO_3)_3$, is an example of the unstable class of compounds, those which liberate large amounts of energy after being given a slight start. Nitroglycerine thus possesses potential energy. Water is an example of the

second class, that of stable compounds; a large amount of energy must be consumed during its decomposition.

163. Heats of Formation Indicate Relative Chemical Stability. + Energy in relation to chemical action is most often measured in terms of heat. It is possible, for example, to cause 23 grams of sodium to unite with 35.5 grams of chlorine (thus forming 1 gram molecule, 58.5 grams, of sodium chloride) in a vessel, called a calorimeter. In this instrument the reaction takes place in an inner chamber so completely surrounded by water that practically all of the heat produced is absorbed by the water. Such an experiment shows that 97,800 grams of water will be raised 1° C. in temperature. This result is expressed briefly by saying that the *heat of formation* of sodium chloride is 97,800 calories. (For definition of calorie, see page 42.)

The heat of formation is the number of calories of heat absorbed or liberated during the formation of a gram-molecular weight of a compound from its elements.

HEATS OF FORMATION OF CERTAIN COMPOUNDS

Aluminum chloride	161,400	Magnesium chloride	151,700
Aluminum oxide	380,000	Mercuric chloride	53,300
Calcium carbide	13,150	Nitrous oxide	−18,000
Carbon disulphide	−19,000	Nitric oxide	−27,600
Copper (cupric) chloride	51,500	Phosphorus pentoxide	370,000
Copper (cupric) sulphate	111,500	Potassium bromide	95,100
Hydrogen chloride	22,000	Potassium chlorate	95,860
Hydrogen bromide	8,446	Potassium chloride	105,700
Hydrogen iodide	−6,400	Potassium iodide	80,130
Hydrogen sulphate	193,300	Silicon carbide	1,963
Hydrogen sulphide	−2,730	Silver oxide	6,500
Iron carbide	8,460	Silver sulphide	3,300
Iron chloride (ferrous)	82,100	Sodium chloride	97,800
Iron chloride (ferric)	96,000	Sodium iodide	69,080
Iron oxide (ferric)	196,500	Sodium sulphide	89,300
Iron sulphate (ferrous)	234,900	Water (liquid)	69,000
Iron sulphate (ferric)	650,500	Zinc chloride	97,300

It is to be noted that the heat of formation may be either negative or positive. The table on page 167 gives heats of formation of a few important compounds. These numbers give reliable indications concerning the stability of the compounds; those having high heats of formation are very stable; those having low values are unstable. Compounds whose heat of formation is negative may be explosive.

164. Types of Chemical Action. There are four chief types of chemical action.

(*a*) *Simple decompositions.* Many compounds are easily separated into their elements, or into simpler compounds, by application of heat or other forms of energy. Examples:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2 \text{ (by use of the electric current)}$$
$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2 \text{ (by heat)}$$

In this type energy must be supplied to make up for that given off when the compound was formed. In general, we can produce a simple decomposition by supplying the needed energy in a form that meets the particular situation.

(*b*) *Direct combinations.* In some cases, elements will unite with each other when brought in contact, either at ordinary temperatures, or on application of a slight amount of energy which serves merely to start the action. Examples:

$$2\,Na + Cl_2 \longrightarrow 2\,NaCl$$
$$C + O_2 \longrightarrow CO_2$$

In these cases energy is given off during the action. By knowing the nature of the elements, we can often tell in advance whether such actions will occur. For example, metals generally tend to react with non-metals.

(*c*) *Single replacements.* In some cases one element displaces another in a compound. Examples:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$2\,H_2O + 2\,Na \longrightarrow 2\,NaOH + H_2$$

We can tell in advance if such actions will occur if we know whether the heat given off in the formation of the new compound from its elements is greater or less than that given off by the second compound when it is formed from its elements (§ 163). In the first example, more heat is given off when zinc chloride is formed from zinc and chlorine than when hydrochloric acid is formed from its elements. Hence we can tell in advance that the action will occur.

(*d*) *Double replacements.* Neutralization is an example of this type of reaction, and other cases are discussed in detail in §§ 167–171.

Begin for tests

165. Reversible Reactions. — We have already had occasion to point out that some chemical actions "work backwards." For example, we may write the equation:

$$3\,Fe + 4\,H_2O \rightleftharpoons Fe_3O_4 + 4\,H_2$$

This reaction goes one way or the other according to the conditions that we establish. If we keep a current of steam passing over hot iron, it proceeds from left to right; if we pass hydrogen over hot iron oxide, it goes from right to left.

Ionizations are also excellent examples of reversible action:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

If we dissolve salt in water, the action goes to the right; if we evaporate water from the solution, the action goes to the left.

166. Dynamic Equilibrium. — In a solution of sodium chloride, provided it is not extremely dilute, we always find undissociated molecules as well as the two kinds of ions. The ratio between the dissociated and the undissociated molecules does not change so long as the volume of the solution and its temperature remain constant. In other words, a condition of equilibrium exists. But there are many reasons for believing that this is not a motionless equilibrium. On the contrary, it is supposed that both the reactions indicated in the above equation are constantly taking place, and that the condition of equilibrium results because the action is proceeding just as fast one way as the other. Thus we have a balanced condition. This is described as *dynamic* (*i.e.* moving) *equilibrium*.

Consider again the action between iron and water. The two constituents are heated in a *sealed* glass tube. Under this condition no substance can escape. Consequently, after a little hydrogen and iron oxide have been formed, they immediately begin to act on each other, independently of the action which produced them, forming iron and water again. In the beginning, the direct action proceeds with the greater speed; but the reverse action gradually gains, until finally they are going with equal speeds, thus balancing each other, so that the action *seems* to stop. Now if we seal equivalent quantities of iron oxide and hydrogen in a second tube and heat them, we arrive at exactly the same result as in the first tube; that is, we have all four substances, iron, iron oxide, water, and hydrogen, and we have them in the same proportion as in the first tube. This fact tends to confirm our belief that the equilibrium reached is dynamic in character.

This conception also explains the condition that exists in many cases where, on mixing two substances, no action

seems to occur, but in which reactions are in reality constantly going on. For example, sodium chloride and potassium nitrate are dissolved in the same solution. Apparently there is no action, but actually there are several cases of equilibrium. At first we have those resulting from the ionization of the two salts:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$KNO_3 \rightleftharpoons K^+ + NO_3^-$$

Then K^+ ions will join with Cl^- ions, giving a new equilibrium:

$$K^+ + Cl^- \rightleftharpoons KCl$$

and Na^+ with NO_3^- will give another:

$$Na^+ + NO_3^- \rightleftharpoons NaNO_3$$

Thus we have in such a solution eight different things present at any instant, and four cases of dynamic equilibrium.

We must note, however, that in this case, as with the sealed tubes, *no product can escape from the field of action.* In cases where one of the products does escape, there can be no reverse action, since at least one of the necessary constituents is lacking.

167. Reactions That Go to an End. — If, in the case of the reactions of iron with water, the tubes had been open, either the steam or the hydrogen would have escaped from the field of action before it could react in the reverse direction. This is what happens if we reduce iron oxide by passing hydrogen over it, or if we pass steam through a tube containing iron. In these cases the reactions continue in one direction until one of the original materials has been entirely used up; such an action is said to *go to an end.*

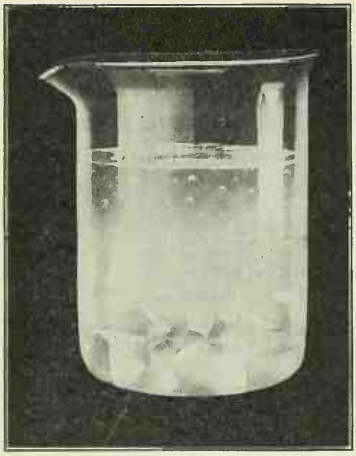


FIGURE 65.

Dilute hydrochloric acid is reacting with marble. The action cannot reverse itself, because carbon dioxide, one of the products, escapes in the form of bubbles of gas. Hence the action goes to an end.

Usually in chemical work we desire that the action shall continue until we obtain as much of the product as possible. In selecting and controlling such actions, the knowledge of reversibility, equilibrium, and the effect of concentration is of great value.

168. Reactions That Go to an End through Volatility. — If at the temperature of the experiment, one of the products of an action is a gas, it will readily escape from the reacting mixture (Fig. 65). The preparation of hydrogen chloride is an excellent example of an action that goes to completion in this way:

$$2\,Na^+ + 2\,Cl^- + 2\,H^+ + SO_4^{--} \longrightarrow 2\,HCl\uparrow + 2\,Na^+ + SO_4^{--}$$

(The arrow pointing upward that follows the formula HCl is a convention, used to indicate that the product formed is volatile, that is, it can pass off as a gas.)

Sulphuric acid is chosen for the reason that its boiling point is so high that there is no possibility of its leaving the mixture at the temperature which will suffice to drive off the hydrogen chloride.

This principle of *volatility* is of practical use in preparing chemical compounds. If the substance we desire is not itself

volatile, we may still employ the principle by selecting our constituents so that another product will be volatile.

169. Reactions That Go to an End through Insolubility. — The ions of an insoluble substance do not separate. An insoluble substance does not, therefore, yield free ions, even though it may be floating in the solvent. Hence, if an insoluble substance is formed in a solvent as the result of a reaction, it is as much out of the field of action as if it had left the mixture. Reactions in which this happens go to an end just as they do when a volatile product is formed. This is one of the most common types of chemical action. As an example, consider the action between solutions of silver nitrate and sodium chloride:

$$Na^+ + Cl^- + Ag^+ + NO_3^- \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$$

(The arrow pointing downward that follows the formula AgCl is a convention used to indicate that the product formed is insoluble and is precipitated in the reaction.)

Silver chloride is insoluble in water. It, therefore, does not separate into ions, and is out of the field of action when once formed. Obviously it cannot play any part in causing a reverse action.

170. Reactions That Go to an End through Non-ionization. — This resembles the preceding case. A substance may form which, although soluble, does not ionize. As far as causing a reverse action is concerned, this substance is out of the field of action. That neutralization actions go to an end is due to this fact. The water, which is invariably formed, is practically non-ionized.

171. Insoluble Substances Used as Tests. — The test for hydrochloric acid or a chloride is a search for the presence of

chlorine ions. The solution of silver nitrate used in the test contains silver ions:

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-$$

If the solution tested contains a chloride, these positive silver ions will encounter negative chlorine ions, and silver chloride is formed. This compound, being practically insoluble and hence undissociated, separates as a precipitate (Fig. 66). Therefore the equation is:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$$

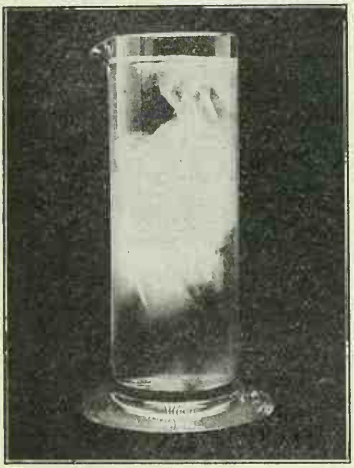


FIGURE 66.

This reaction between silver nitrate solution and hydrochloric acid goes to an end because silver chloride, being insoluble, leaves the field of action in the form of a precipitate.

The complete equation for such a test would be:

$$Na^+ + Cl^- + Ag^+ + NO_3^- \longrightarrow AgCl\downarrow + Na^+ + NO_3^-$$

A solution of potassium chlorate also contains chlorine, not as a simple ion, but as part of the ion ClO_3^-. So when we mix this solution with the silver nitrate, we have the ions Ag^+, NO_3^-, K^+, ClO_3^-. Here no precipitation takes place, for although the compounds, silver chlorate, $AgClO_3$, and potassium nitrate, KNO_3, both form, they are both soluble and the reaction reaches equilibrium. Silver nitrate solution, then, is the test for the chlorine *ion*, and not for the chlorine *atom*.

The test for a sulphate depends upon the combination of barium ions, Ba^{++} (from the barium chloride added), with

the SO_4^{--} ion of the sulphate. The barium sulphate formed is insoluble and separates as undissociated molecules. The equation is:

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4 \downarrow$$

These tests furnish good examples of reactions that go to an end through insolubility.

172. Law of Mass Action. — The theory of moving particles can also be employed to make clear some matters connected with ionization and equilibrium. In a solution, both ions and molecules are in constant movement, and there are constant collisions between the particles. As a result, some gain momentum while others lose it, until finally the particles have widely different velocities. In a case where there exists a dynamic equilibrium like that shown in the equation:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

the reactions in the two directions are affected by the nature of the collisions which occur. If a molecule of sodium chloride meets with a violent impact, its ions may be separated; while two oppositely charged ions may meet in such a way as to unite them. Thus the reactions in the two different directions are accounted for.

Next we will consider an experiment. To a saturated solution of common salt we add hydrogen chloride gas. This in dissolving tends to reach the equilibrium:

$$HCl \rightleftharpoons H^+ + Cl^-$$

It thus gives more Cl^- ions, like those that were already in solution. In other words, we increase the *concentration* of the chlorine ions. As an experimental result of the addi-

tion, we observe that sodium chloride is precipitated in the form of fine crystals.

The following is the explanation of this action. By increasing the number of chlorine ions in the solution, we increase the number of impacts between the Na^+ and Cl^- ions and consequently the chance of forming more sodium chloride molecules. Since the solution is already saturated with these, the newly formed ones must go out of solution and be precipitated. A similar result may be obtained if we add a substance, like sodium nitrate, which would increase the concentration of the Na^+ ions. Thus, in general, we can increase the speed of a chemical action by increasing the impacts between the substances which produce the action. This occurs when the concentration of even one of the substances is increased; and in these cases the action goes further toward completion.

The law which states these generalizations is known as the *Law of Mass Action*. In its full form it gives the mathematical relations of the concentrations, but for our purposes we can state it as follows: *The speed of a chemical action is increased in a given direction by increasing the concentration of one of the substances that produce the action.*

173. Applications of the Law of Mass Action. — These are of very great importance, since the principle, like those involved in ionization and equilibrium, is of general application. Chemical actions that go to an end are themselves examples of the operation of the law. When a substance leaves the field of action through its insolubility, volatility, or non-ionization, the concentration of that substance becomes zero, and there can be no impacts between it and another substance tending to produce a reverse action.

But most actions do not go to an end. Control in such cases is often secured through a knowledge of the principle of mass action. Perhaps the most important examples are those involving a substance that is almost, but not wholly, insoluble. Barium sulphate is a compound of this kind. Therefore the reaction:

$$Ba^{++} + 2\,Cl^- + 2\,H^+ + SO_4^{--} \longrightarrow BaSO_4\downarrow + 2\,H^+ + 2\,Cl^-$$

goes only approximately to an end. But it is often necessary to precipitate barium as a sulphate as completely as possible. The principle of mass action points a way to accomplish this, by the addition of a considerable excess of sulphuric acid when producing the precipitation. The concentration of the SO_4^{--} ions is thereby increased, and almost all the Ba^{++} ions are brought into action to produce molecular barium sulphate.

The sour taste and chemical activity of an acid are due to the presence of hydrogen ions. As hydrogen ions are removed by combining with the hydroxyl ions of a base, other molecules of the acid dissociate, so that other hydrogen ions form, which will in turn unite with additional hydroxyl ions. These processes of dissociation and combination continue until all of the replaceable hydrogen of the acid has been neutralized. Molecules of weak acids *do not dissociate* into ions readily, but molecules of the soluble salts of weak acids *are ionized* readily. The concentration of the acid radical ion in a solution, therefore, can be increased by the addition of a soluble salt of a weak acid to a water solution of that acid. A weak acid becomes practically inactive in the presence of a solution of one of its own salts. The addition of a salt of a strong acid does not appreciably affect the ionization of the acid.

SUMMARY

Compounds with high positive **heats of formation** are stable; those with negative heats of formation are likely to be unstable.

The four chief types of chemical action are:

(a) **Simple decompositions**; (b) **direct combinations**; (c) **single replacements**; (d) **double replacements.**

Chemical actions in general are **reversible**; hence, unless special conditions are established, two substances do not give complete reaction with each other on being mixed. A reverse action sets in, and both it and the direct action continue simultaneously. A state of **dynamic equilibrium** thus exists.

Where reactions do not remain in a state of dynamic equilibrium but do **go to an end**, it is because one of the products **leaves the field of action.** This may happen through **insolubility, volatility,** or **non-ionization.**

Most of the reactions of the laboratory are chosen so that they will **go to an end** through the operation of one of these principles.

Tests for chlorides, sulphates, and other ions are good examples of actions that go to an end through **insolubility.**

The preparation of hydrogen chloride is a good example of an action that goes to an end through **volatility.**

Neutralizations go to an end because the water that is formed is practically **non-ionized.**

The character of the equilibrium in a given chemical action can be controlled through the **Law of Mass Action,** which states: **The speed of a chemical reaction is increased in a given direction by increasing the concentration of one of the substances that produce the action.**

Examples of the practical application of the law of mass action are found in the facts that (*a*) a slightly soluble substance can be almost completely precipitated by adding an excess of one of the ions that help to form it, and (*b*) that weak acids are less active in the presence of their own salts, because the salts of these acids are generally much more highly ionized than the acids themselves.

EXERCISES

1. The cases listed below represent reactions, some of which occur under ordinary conditions, some that can be made to proceed by application of heat or other forms of energy, and some that cannot be made to occur at all by any ordinary methods within our power. Make a judgment in each case, giving reasons for your prediction. In case you think no reaction will take place, write "No reaction." In the other cases, write a complete balanced chemical equation and state whether ordinary or special conditions are necessary, naming the latter. Heats of formation given on page 167 will aid in most cases. Name the type of chemical action represented.

(*a*) chlorine + oxygen ⟶
(*b*) oxygen + hydrogen sulphide ⟶
(*c*) iron oxide (heated) ⟶
(*d*) iron oxide + chlorine ⟶
(*e*) gold + hydrogen ⟶
(*f*) zinc chloride + hydrogen ⟶
(*g*) sulphur + hydrogen ⟶
(*h*) sodium chlorate (heated) ⟶
(*i*) iron sulphate + hydrogen ⟶
(*j*) sodium chloride + zinc ⟶
(*k*) sodium + sulphur ⟶
(*l*) iron + zinc ⟶
(*m*) aluminum + oxygen ⟶
(*n*) aluminum + chlorine ⟶
(*o*) iron oxide + aluminum ⟶
(*p*) hydrogen sulphide + nitrogen ⟶
(*q*) sulphuric acid + chlorine ⟶
(*r*) chlorine + copper ⟶
(*s*) potassium chloride (heated) ⟶
(*t*) sulphur + silver ⟶

2. What is meant by reversible reactions? Give three examples.

3. Explain the meaning of the word *dynamic* in the phrase *dynamic equilibrium.*

4. Write an equation to show that the ionization of potassium nitrate is a reversible reaction. Under what conditions can the speed be increased, reading from left to right? From right to left?

5. Write an equation to show the ionization of copper sulphate in water solution. Does this represent an action that goes to an end? Explain.

6. Mention three conditions under which actions go to an end. Explain.

7. By reference to the Table and Rules for Solubility and Volatility in the Appendix, determine which of the following reactions go to an end, and which rest in a state of equilibrium. State the reason in each case, and complete the equation in case the reaction goes to an end:

$HgNO_3 + KCl \longrightarrow$
$CuSO_4 + NaNO_3 \longrightarrow$
$Na_2CO_3 + HNO_3 \longrightarrow$
$NaBr + H_2SO_4 \longrightarrow$
$BaCl_2 + CuSO_4 \longrightarrow$
$ZnS + H_2SO_4 \longrightarrow$
$Na_2SO_4 + HCl \longrightarrow$
$NaOH + HNO_3 \longrightarrow$
$KNO_3 + Na_2SO_4 \longrightarrow$
$CaCl_2 + Na_2CO_3 \longrightarrow$

$Na_2SO_3 + H_2SO_4 \longrightarrow$
$Pb(NO_3)_2 + Na_2SO_4 \longrightarrow$
$NH_4Cl + NaOH \longrightarrow$
$Zn(NO_3)_2 + H_2SO_4 \longrightarrow$
$FeCl_3 + K_2SO_4 \longrightarrow$
$Pb(NO_3)_2 + CuCl_2 \longrightarrow$
$FeS + H_2SO_4 \longrightarrow$
$NaNO_3 + HCl \longrightarrow$
$AgNO_3 + FeCl_3 \longrightarrow$
$CaCO_3 + HCl \longrightarrow$

8. Write equations to show three ways of making potassium nitrate, illustrating each of the three ways in which reactions may go to an end.

9. State the Law of Mass Action.

10. Lead sulphate is slightly soluble in water. What could be added to make it less soluble? Explain.

11. Is common salt as soluble in a dilute solution of hydrochloric acid as it is in water? Explain.

12. Which is the more ionized in water solution, a weak acid or its sodium salt?

13. If sodium acetate is present in a solution of acetic acid, what is the effect on the activity of the acid?

14. Why does the zinc in a hydrogen generator dissolve less rapidly after a time, even though there is still an excess of sulphuric acid present?

15. Hydrogen and the magnetic oxide of iron react according to the reversible equation:

$$Fe_3O_4 + 4\ H_2 \rightleftarrows 3\ Fe + 4\ H_2O$$

How may the direction of the reaction be controlled? How may dynamic equilibrium be established?

16. Calcium sulphate is but slightly soluble in water. Why is it difficult to dissolve much calcium carbonate in dilute sulphuric acid?

CHAPTER XV

SODIUM AND POTASSIUM COMPOUNDS

174. General Properties. — Sodium and potassium compounds may be studied together advantageously, as the corresponding compounds that the two elements form are very similar.

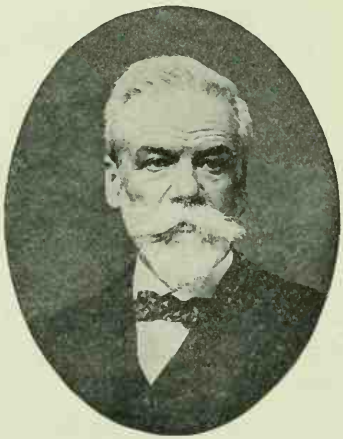
Most sodium and potassium compounds are white crystalline substances; practically all of them are soluble in water. With the exception of sodium peroxide and the hydroxides, all of those that we shall study are salts, possessing in a marked degree those properties that are characteristic of this class of bodies. As a rule, they are very stable compounds. They are among our most common and useful substances.

Sodium compounds are generally less soluble in water than are the corresponding potassium compounds; they are, therefore, not so satisfactory for certain uses. On the other hand, sodium salts are usually cheaper than those of potassium. Moreover, since the atomic weight of sodium is 23, while that of potassium is 39, a gram of a sodium salt contains a greater number of molecules than a gram of the corresponding potassium compound. Consequently, a gram of a sodium salt will "go farther" than a gram of the corresponding potassium salt. For these reasons, sodium compounds are generally used in manufacturing operations in preference to those of potassium. In describing the preparations, the sodium compound will be taken as a type for both.

175. Sodium Hydroxide. — The manufacture of sodium hydroxide by the electrolysis of sodium chloride is closely

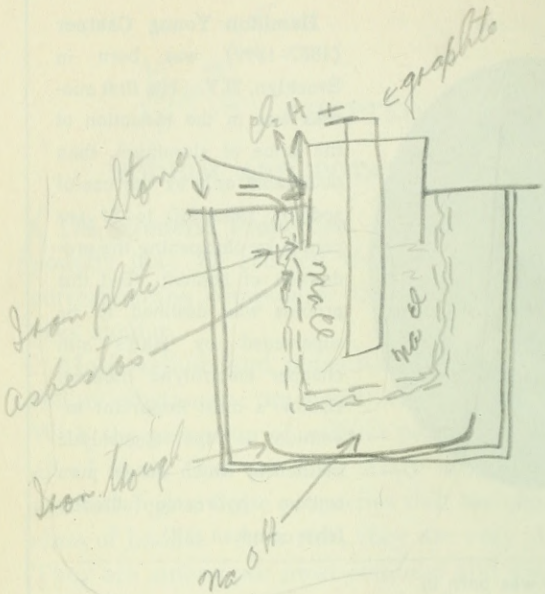
Hamilton Young Castner (1857–1899) was born in Brooklyn, N.Y. His first success was in the reduction of the price of aluminum, then obtainable only by the use of sodium, from $10 to $1 per pound, by cheapening the production of sodium. But this process was destined to be superseded by Hall's still cheaper electrolytic method. Castner's most important invention is the electrolytic method by which we get pure sodium hydroxide directly from common salt.

Ernest Solvay was born in Belgium in 1839 and still lives in Brussels. He made practical a process for obtaining the carbonates of sodium directly from common salt by a precipitation method. His process is the only one used in this country. Solvay has received many honors and great wealth as a result of his discovery. He has been prominent in the political life of his country and has been a member of the Belgian Senate.



Nelson Cell

$2NaCl + 2H_2O \rightarrow Cl_2 \uparrow + 2NaOH + H_2$



associated with the manufacture of chlorine. As already stated, a water solution of sodium chloride when electrolyzed yields chlorine, sodium hydroxide, and hydrogen, according to the equation:

$$2\,NaCl + 2\,H_2O \longrightarrow Cl_2\uparrow + 2\,NaOH + H_2$$

The products of this reaction must not be allowed to mix, lest complicated secondary reactions take place.

One apparatus for this process has been described (§ 85). Whether chlorine or sodium hydroxide is considered as a by-product depends on whether the preparation of chlorine or sodium hydroxide is the chief object of the electrolysis.

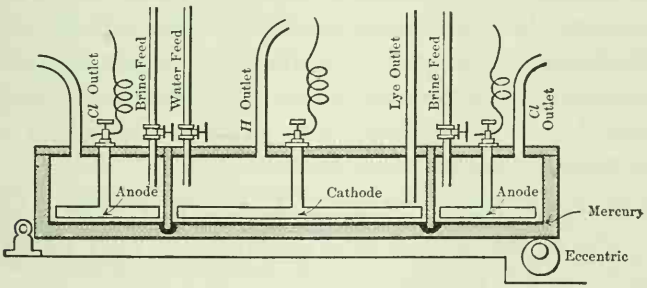


FIGURE 67.

An electric current flows through a solution of sodium chloride in this device. The thin layer of mercury which oscillates back and forth acts as a cathode while in the outer compartments, and dissolves the sodium as it is liberated. On reaching the middle compartment the dissolved sodium reacts with water. There are three final products: sodium hydroxide, hydrogen, and chlorine.

176. Castner Process. — For carrying out the reaction given above, the apparatus (Fig. 67) consists of a stone cell, divided into three compartments. The end compartments contain a concentrated solution of salt. The middle compartment contains a dilute solution of sodium hydroxide. A layer of mercury covers the bottom of the cell, passing

under the partitions. The mercury is made to flow backward and forward by rocking the apparatus by means of an eccentric.

The current passes from the carbon anode through the salt solution to the mercury, and then from the mercury through the sodium hydroxide solution to the iron cathode. This makes the mercury negative relative to the anodes, and positive relative to the cathode. Chlorine ions pass to the anodes, where chlorine gas is liberated and drawn from the apparatus. The sodium ions pass to the mercury, where they become sodium atoms and form sodium amalgam. This is carried by the rocking of the tank to the middle compartment, where the sodium reacts with water to form sodium hydroxide and hydrogen. The solution of sodium hydroxide is drawn off, the water evaporated, and the sodium hydroxide obtained pure as a white solid. This is melted and cast into sticks, or run into iron drums.

177. Lye Process. — Calcium hydroxide, $Ca(OH)_2$, ordinary slaked lime, is made from calcium oxide, CaO, unslaked lime, by adding water:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Calcium hydroxide is slightly soluble in water. If a solution of it is boiled with sodium carbonate, Na_2CO_3, the following reaction occurs:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2\,Na^+ + 2\,OH^-$$

The calcium carbonate, $CaCO_3$, formed is insoluble. It is this fact that makes the action go to an end. The solution containing the sodium and hydroxyl ions is separated from the precipitated calcium carbonate and evaporated to produce sodium hydroxide.

178. Properties of the Hydroxides. — Sodium and potassium hydroxides are very strong bases. As we have seen, they neutralize acids, forming salts and water. These bases have such a corrosive action on animal and vegetable matter that they are said to be *caustic*. Solutions of either sodium hydroxide or potassium hydroxide readily dissolve silk and wool. Dilute solutions of these alkalies have little effect on cotton, but warm concentrated solutions react with the cotton fiber. Glass is attacked by these hydroxides; and, although the action is somewhat slow, a solution of either hydroxide on standing in a glass bottle becomes quite impure and causes a glass stopper to stick. Both sodium and potassium hydroxides are very deliquescent substances. One of their most useful properties is their ability to react with animal and vegetable fats and oils to form soaps.

179. Uses. — Sodium hydroxide, commonly called *caustic soda*, is manufactured in enormous quantities for use in soap making. It is used in making sodium hypochlorite for bleaching solutions, and is the soda lye used in the manufacture of wood pulp for paper-making. Sodium hydroxide is a cheap, strong base, used in many industries. Potassium hydroxide, *caustic potash*, is not so extensively used in manufacturing operations. It is used to make other compounds of potassium, and in the preparation of some soaps.

180. Sodium Peroxide. — This compound is made by heating chips of sodium in air freed from carbon dioxide:

$$2\,Na + O_2 \longrightarrow Na_2O_2$$

The temperature for the reaction must be kept between 300° C. and 400° C.

Sodium peroxide reacts violently with water, producing sodium hydroxide and oxygen:

$$2\,Na_2O_2 + 2\,H_2O \longrightarrow 4\,NaOH + O_2 \uparrow$$

When the reaction is carefully regulated, it is a most convenient laboratory method for making small quantities of oxygen. Sodium peroxide should never be left on paper or other combustible material, as the heat of reaction with moisture may cause a blaze. Sodium peroxide is useful for making solutions of hydrogen peroxide for the laboratory, by sifting the powder into very dilute acid solutions:

$$Na_2O_2 + 2\,HCl \longrightarrow H_2O_2 + 2\,NaCl$$

The use of sodium peroxide as an oxidizing and bleaching agent is increasing.

FIGURE 68.

Sodium chloride, common salt, as found in mines. The mineral name is halite.

181. Sources of Sodium Chloride. — Sodium chloride, NaCl, *common salt*, is the most abundant sodium compound found in nature. Rock salt, or halite (Fig. 68), is found in many countries, but the largest deposits are those in New York (Fig. 69), Louisiana, Austria, Jugo-Slavia, Germany, and Spain. Often in these beds the salt is of such purity that it has only to be mined and crushed to be ready for use.

Much of the salt of this country is obtained from salt wells in New York, Michigan, Ohio, and other states. Several borings are made and water sent down some of them (Fig. 70, *a*) to the salt bed. There brine is formed and forced, or

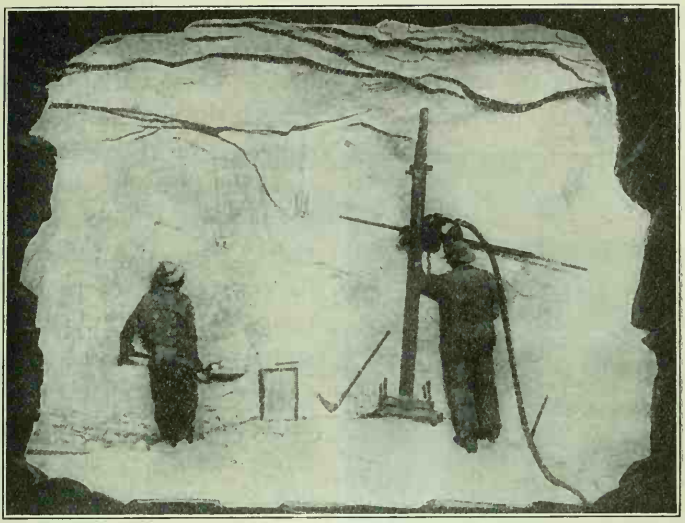


FIGURE 69.

Common salt is sometimes obtained from mines. It must be drilled and blasted like rock. This mine is at Retsof, New York.

pumped, through other borings (*b*) to the surface. The earthy impurities in the brine settle, and then it is evaporated, usually under reduced pressure. A fairly pure salt is thus obtained.

The total amount of salt found in deposits, however, is insignificant compared with the quantity contained in the seas and oceans. The percentage of salt in sea water is small,

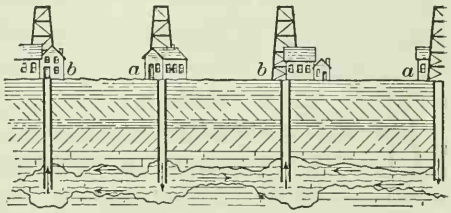


FIGURE 70.

How common salt is dissolved from its beds under the surface of the earth. Water is forced down through wells *a* and salt water is pumped up through wells *b*.

yet it has been computed that the total quantity in the sea is 36,000,000,000,000,000 tons. The percentage of salt is not uniform for all seas and oceans. These variations depend upon the relation existing between the amount of water delivered by rivers to a sea and the amount lost by evaporation. Thus, in the Baltic Sea, the inflow of river water, which contains much less salt than sea water, exceeds the loss by evaporation. Hence the water of the Baltic is relatively fresh. In the Dead Sea the reverse conditions prevail; evaporation exceeds the inflow, and a solution approaching saturation has resulted. The average amounts of salts contained in one hundred parts of sea water are:

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FIGURE 71.

In warm countries the heat of the sun is sometimes used to evaporate water from diked-in, shallow basins of the sea. Crude salt is thus obtained.

Dead Sea . . .	22.0 parts	Atlantic Ocean .	3.6 parts
Mediterranean .	3.8 parts	Baltic	0.5 part

182. Extraction of Salt from Sea Water. — The method employed for getting salt from sea water depends upon the climate. In warm countries the sea water is evaporated by the sun's heat in shallow basins (Fig. 71). The salt that thus crystallizes is not very pure. In cold countries like northern Russia, sea water is allowed to freeze in flat basins. The coating of ice, which contains very little salt, is removed,

and the process is repeated till a concentrated brine is obtained which it will pay to evaporate by artificial heat to secure the salt.

183. Properties and Uses of Sodium Chloride. — Sodium chloride crystallizes in transparent cubes. Generally these cubes arrange themselves in four-sided, hollow pyramids, known as *hopper crystals* (Fig. 72). Sodium chloride is but slightly more soluble in hot water than in cold. It vaporizes slowly at a red heat.

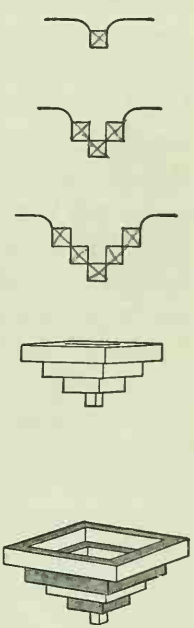


FIGURE 72.
Common salt is often seen as hopper shaped crystals. This diagram shows how they develop.

Sodium chloride is typical of one of the three great classes of chemical compounds. It was the first representative of its class to become familiar to man. Other compounds with properties similar to common salt became known as *salts*. For a long time the term *salt* meant a white substance soluble in water, with a taste resembling common salt. Many compounds now known as salts possess neither of these properties. A water solution of a neutral salt, like sodium chloride, does not change the color of litmus. Like most salts, sodium chloride is composed of a metallic element and a non-metallic constituent.

Salt is indispensable as a food for the higher animals. It furnishes the chlorine needed for the hydrochloric acid in the gastric juice. Thousands of tons of common salt are used every year in the preparation of sodium carbonate and

sodium hydroxide. Enormous quantities of salt are consumed in ice-cream making and other refrigeration, and in preserving meat and fish for future use as food.

Common salt contains several impurities. The principal impurity is magnesium chloride, a deliquescent substance that causes ordinary salt to cake. To remedy this defect, various substances such as starch, flour, and sodium bicarbonate are added.

184. Potassium Compounds. — Potassium is one of the elements essential to plant life. Potassium compounds that can be taken up by the roots of plants must be present in the soil in which plants are grown. Before the war the United States imported from Germany for use in agricultural fertilizers potassium compounds, chiefly potassium chloride and potassium sulphate, equivalent to about 200,000 tons of "potash," K_2O, each year. The sudden ending of this supply when war was declared, created a problem that had to be met immediately in order to prevent a serious decrease in the fertility of the farm lands of the United States. It was found that other substances could be substituted for the potassium compounds used in most industries, but not for those used in fertilizers.

An extensive search was made in this country for potassium compounds, and many sources of potash were found. The most promising of these are the recovery of potash from the flue dust of cement works and from the dust of iron blast furnaces, the evaporation of the brines of lakes, located chiefly in California and Nebraska, and the separation of potassium compounds from kelp. Less important methods of obtaining potassium compounds are (*a*) from wood ashes, (*b*) as a by-product of the sugar-beet industry, (*c*) from the

water used for washing wool, and (*d*) by the decomposition of silicate rocks containing combined potassium.

When the war ended, the potash industry was well started in this country, and there is little doubt that it could have been developed to meet all the demands of the nation for potassium compounds. The most important deposits of soluble potassium compounds are located at Stassfurt, Germany. To compete successfully with Germany, the United States must produce its potash as a by-product of paying industries.

185. Preparation of the Carbonates (Na_2CO_3, $NaHCO_3$). — These important compounds occur only to a very limited extent in nature. The ashes of land plants contain potassium carbonate, and the ashes of sea plants, both sodium and potassium carbonates. Since the supply is so limited, the manufacture of sodium carbonate from common salt is of enormous importance.

The process now used is the *Solvay process*, and may be considered as taking place in the following steps.

The gas ammonia, NH_3, unites with water to form ammonium hydroxide:

(1) $$NH_3 + H_2O \longrightarrow NH_4OH$$

Carbon dioxide unites with water to form carbonic acid, H_2CO_3:

(2) $$CO_2 + H_2O \longrightarrow H_2CO_3$$

When ammonium hydroxide is brought in contact with an excess of carbonic acid, all of the OH^- ions of the base unite with H^+ ions from the acid and the solution will contain ammonium hydrogen carbonate (ammonium bicarbonate):

(3) $$NH_4^+ + OH^- + 2\,H^+ + CO_3^{--} \longrightarrow H_2O + NH_4^+ + HCO_3^-$$

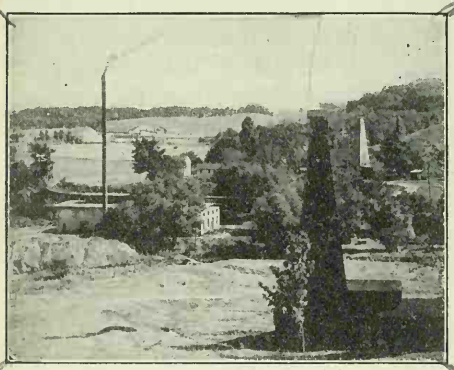
When concentrated solutions of ammonium bicarbonate and sodium chloride are mixed, sodium bicarbonate will separate, because it is only slightly soluble under the conditions of the experiment:

(4) $NH_4^+ + HCO_3^- + Na^+ + Cl^- \longrightarrow NaHCO_3\downarrow + NH_4^+ + Cl^-$

The above considerations may aid in obtaining equation (5), generally written to represent the Solvay process. Equation (5) is the sum of equations (1), (2), (3), and (4).

(5) $NaCl + H_2O + CO_2 + NH_3 \longrightarrow NaHCO_3\downarrow + NH_4Cl$

In practice, the operation is carried out by saturating a concentrated brine with ammonia and then passing carbon dioxide into this mixture under pressure.



Courtesy of the Solvay Process Co.

FIGURE 73. — SALT WELLS NEAR SYRACUSE, N. Y. These furnish sodium chloride brine which is used in making sodium carbonate.

The sodium bicarbonate is separated by filtration and purified. The impure sodium bicarbonate, remaining after the filtration of the liquid, is washed with water, dried, and then heated to drive off volatile impurities and to convert it into pure sodium carbonate:

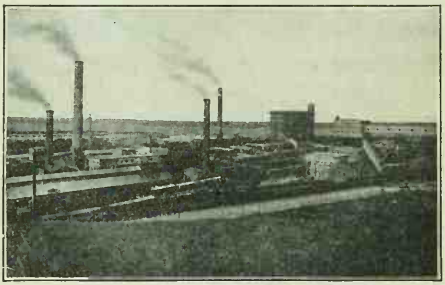
$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2\uparrow$$

The pure sodium carbonate thus obtained may be: (*a*) placed on the market as anhydrous sodium carbonate (soda ash); (*b*) crystallized from water solution and sold as

washing soda, $Na_2CO_3 \cdot 10\,H_2O$; (*c*) reconverted into pure sodium bicarbonate, baking soda, $NaHCO_3$:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\,NaHCO_3$$

It is a matter of great importance to produce sodium carbonate at low cost. For this reason the above reactions are carried out so that the by-products are utilized. The ammonium chloride is used to furnish ammonia to saturate a fresh supply of brine. The carbon dioxide that is given off in decomposing sodium bicarbonate furnishes part of the supply of that gas needed in the preparation of the pure sodium bicarbonate.



Courtesy of the Solvay Process Co.

FIGURE 74.

A huge plant where common salt is converted into washing soda and baking soda.

186. Uses of the Carbonates. — Two uses of the carbonates of sodium have been implied in the names "washing soda" and "baking soda." Sodium carbonate, often called "soda," has in a modified way the properties of sodium hydroxide. Large quantities of sodium carbonate are used in glass making. In the refining of petroleum, sodium carbonate is used to neutralize sulphuric acid that is employed in a preliminary part of the process. It reacts with many substances, especially oils or fats, making soluble compounds, and hence it is an excellent cleansing substance. It is usually an important constituent of soap powders. Both washing soda and baking soda liberate carbon dioxide when treated with acids:

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2\uparrow$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

Since the molecular weight of the carbonate is 106 and that of the bicarbonate 84, there will be more molecules of the bicarbonate than of the carbonate in equal weights of the two substances. From these facts we see that, for equal weights of the carbonates, baking soda furnishes the greater amount of carbon dioxide. It is consequently preferred for those uses in which the liberation of carbon dioxide is required, as in baking powder.

Sodium bicarbonate is used in chemical fire extinguishers, is an important constituent of baking powders, and is used in the manufacture of effervescent salts.

187. Hydrolysis. — Many salts, even when carefully purified, form solutions that are not neutral to litmus. Solutions of sodium carbonate turn red litmus blue; solutions of copper sulphate turn blue litmus red. In explaining the action it will be necessary to consider the base and the acid from which the salt is either actually or theoretically derived. The following table gives data for several cases:

Salt in Solution	Turns Litmus	Acid	Base	Comparative Strength of the Acid and Base
Sodium carbonate, Na_2CO_3	blue	H_2CO_3	NaOH	Base strong, acid weak
Potassium carbonate, K_2CO_3	blue	H_2CO_3	KOH	Base strong, acid weak
Sodium tetraborate, $Na_2B_4O_7$	blue	$H_2B_4O_7$	NaOH	Base strong, acid weak
Zinc chloride, $ZnCl_2$	red	HCl	$Zn(OH)_2$	Base weak, acid strong
Copper sulphate, $CuSO_4$	red	H_2SO_4	$Cu(OH)_2$	Base weak, acid strong
Aluminum sulphate, $Al_2(SO_4)_3$	red	H_2SO_4	$Al(OH)_3$	Base weak, acid strong
Sodium sulphate, Na_2SO_4	neutral	H_2SO_4	NaOH	Base and acid, both strong
Potassium chloride, KCl	neutral	HCl	KOH	Base and acid, both strong

We note that when the base is much stronger than the acid, the salt solution turns litmus blue, that when the acid is much stronger than the base, the salt solution turns litmus

red, and that when the two constituents match each other, the salt is neutral.

The explanation of the fact that solutions of the first two classes of salts are not neutral lies in the supposition that *neutralization reactions reverse themselves to a slight extent*, because water ionizes in a small degree:

$$H_2O \rightleftarrows H^+ + OH^-$$

Ordinarily this very slight ionization of water plays no part in chemical actions, but an exception exists in the cases that we have noted. On dissolving sodium carbonate, for example, the following cases of equilibrium exist:

$$Na_2CO_3 \rightleftarrows 2\,Na^+ + CO_3^{--}$$
$$H_2O \rightleftarrows H^+ + OH^-$$

The four ions Na^+, CO_3^{--}, H^+, OH^- immediately tend to make new equilibriums:

$$Na^+ + OH^- \rightleftarrows NaOH$$
$$2\,H^+ + CO_3^{--} \rightleftarrows H_2CO_3$$

Sodium hydroxide, being a strong base, has a great tendency to dissociate; hence the first of these actions tends to proceed to the left. Carbonic acid, being a weak acid, has but slight tendency to dissociate, and hence the second action tends towards the right. In other words, more hydrogen ions than hydroxyl ions are withdrawn from the solution. The hydroxyl ions remain in the solution in greater number, and the result is that litmus is turned blue. The practical effect is to reverse the neutralization equation of the salt, thus:

$$Na_2CO_3 + 2\,H_2O \longrightarrow 2\,Na^+ + 2\,OH^- + H_2CO_3$$

The acid reaction of copper sulphate solution is explained in a similar manner. The original equilibriums are:

$$CuSO_4 \rightleftarrows Cu^{++} + SO_4^{--}$$
$$H_2O \rightleftarrows H^+ + OH^-$$

The secondary equilibriums are:

$$Cu^{++} + 2\ OH^- \rightleftarrows Cu(OH)_2$$
$$2\ H^+ + SO_4^{--} \rightleftarrows H_2SO_4$$

The base, copper hydroxide, has little tendency to dissociate; the sulphuric acid has a great tendency to dissociate. Hence the hydroxyl ions are withdrawn in greater number than the hydrogen ions, and the solution shows an acid action. A reverse of neutralization occurs:

$$CuSO_4 + 2\ H_2O \longrightarrow 2\ H^+ + SO_4^{--} + Cu(OH)_2$$

The actions of water with such salts as sodium carbonate and copper sulphate are cases of hydrolysis.

Hydrolysis is a reversal of neutralization.

It operates to produce a solution that turns litmus blue in the case of salts that are derived from a combination of a weak acid with a strong base; it operates to produce a solution that turns litmus red in the case of a salt derived from a strong acid with a weak base.

When the base and acid are of approximately the same strength, both hydrogen ions and hydroxyl ions are withdrawn in the same degree, and the solution of the salt is neutral, and no perceptible result of the hydrolysis occurs.

188. Occurrence of the Nitrates ($NaNO_3$, KNO_3). — Both sodium and potassium nitrates occur in small quantities in the soil. They are formed by nitrogenous organic matter decaying in contact with soluble sodium or potassium compounds.

Deposits of sodium nitrate, covering an area of over four hundred square miles, are found in desert regions along the western coast of South America. These beds lie near the boundary lines of Peru, Chile, and Bolivia, and have been the cause of many disputes between these countries. The crude nitrate is obtained from the loose material of the beds by heating it in water. The liquor containing the nitrate is run off and allowed to crystallize. The product, crude Chile saltpeter, contains 94% to 98% of sodium nitrate. A purer quality of sodium nitrate is obtained by recrystallization (Fig. 75).

FIGURE 75.
A crystal of sodium nitrate.

189. Manufacture of Potassium Nitrate.—This potassium compound is made by mixing hot concentrated solutions of sodium nitrate and potassium chloride. The equation for the reaction is:

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl\downarrow$$

On evaporation, the boiling mixture first deposits common salt, since this substance is less soluble in boiling water than is potassium nitrate. On cooling the solution, however, the potassium nitrate crystallizes out, because it is far less soluble in cold than in hot water. A purer quality of potassium nitrate can be obtained by recrystallization.

190. Properties of the Nitrates. — Sodium and potassium nitrates are white, soluble salts. Sodium nitrate differs from the potassium compound in crystalline form and in being more hygroscopic. Both nitrates give off oxygen

when heated, and leave compounds containing less oxygen, known as nitrites:

$$2\ NaNO_3 \longrightarrow 2\ NaNO_2 + O_2$$

191. Uses. — The cheaper sodium nitrate is used in the manufacture of nitric acid and its derivatives. Chile saltpeter is also used as a fertilizer, and in the manufacture of sodium nitrite, a most important substance in the manufacture of aniline dyes. The principal use of potassium nitrate (ordinary saltpeter) is in the manufacture of black gunpowder. Potassium nitrate is also used to preserve meat, and corned beef owes its red color to this treatment.

SUMMARY

The **hydroxides** of sodium and potassium are prepared by the electrolysis of solutions of the chlorides, and by the reaction of the carbonates with slaked lime.

Sodium **peroxide** is made by burning sodium in air. It is used as an oxidizing agent.

The **chlorides** of these two metals occur in nature. They are typical salts. They have a saline taste, are neutral, and result from the neutralization of the corresponding acid and base.

They are used in the preparation of other sodium and potassium compounds.

The **bicarbonates** are made commercially by the action of carbon dioxide with ammoniacal solutions of the chlorides. They are only slightly soluble and are less corrosive than the carbonates.

Sodium bicarbonate is a constituent of all baking powders and is used in chemical fire extinguishers.

The **carbonates** occur in plant ashes. They are commercially prepared by the decomposition of the bicarbonates by heat.

The carbonates are used in the preparation of soaps, washing powders, glass, and in making other compounds.

Sodium nitrate is obtained from Chile. **Potassium nitrate** is formed by the reaction of potassium chloride with sodium nitrate.

Sodium nitrate is used to prepare potassium nitrate, also as a fertilizer, and as a source of nitric acid. Potassium nitrate is used in gunpowder.

EXERCISES

1. How could you show that there are potassium compounds in plants?

2. Describe one process used for the preparation of sodium hydroxide.

3. Compare the properties of sodium hydroxide with those of potassium hydroxide.

4. What oxide is made by burning sodium in air? For what is this oxide used?

5. How many liters of oxygen could be obtained from 30 grams of sodium peroxide by its reaction with water?

6. Give examples to show that salt is of great importance to chemical industries.

7. Mention three ways in which salt is obtained.

8. Why does table salt "cake"?

9. Why was sodium carbonate obtained from the ashes of sea plants and not from the water directly?

10. Write the equations for the preparation of sodium carbonate by the Solvay process.

11. In getting sodium *carbonate*, in the Solvay process, why do we have to get the *bicarbonate* first and then decompose it?

12. What advantage has baking soda over potassium bicarbonate?

13. Equal weights being taken, which will neutralize the larger quantity of acid, sodium hydroxide or potassium hydroxide? Sodium carbonate or bicarbonate? Explain.

14. Why is "soda" used in cleaning?

15. What objection is there to using solutions of washing soda to cleanse woolen goods?

16. How could you distinguish chemically between washing soda and baking soda?

17. Would a water solution of sodium bicarbonate give an alkaline or an acid reaction? Explain.

18. How could you distinguish between potassium nitrate and sodium nitrate?

19. How are the nitrates produced in nature?

20. Why can potassium nitrate be obtained by a reaction between potassium chloride and sodium nitrate?

21. Why should the potash industry of the country be developed?

22. How much sodium carbonate could be obtained from a ton of sodium bicarbonate?

23. How would solutions of the following salts affect litmus: sodium acetate, zinc sulphate, copper nitrate, aluminum chloride, potassium nitrate? Give reasons for your answers.

CHAPTER XVI

SULPHUR AND SULPHIDES

192. Occurrence. — Sulphur is found in nature either free or in combination with other elements. In the uncombined or *native* state it is found in volcanic regions. The most extensive deposits of native sulphur are the Louisiana and Texas beds, where the sulphur is found several hundred feet below the surface. These beds furnish annually not only enough sulphur to supply the United States but about half a million tons for export.

Sulphur is found combined with many different metals, as *sulphides;* those of iron, copper, lead, and zinc are the more abundant. The *sulphates* of a few metals are found in considerable quantities.

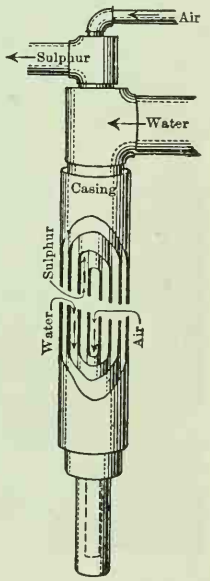


FIGURE 76.

Showing how heated water and air are carried to the sulphur beds, and how another pipe placed between them provides a path through which the frothy mixture of melted sulphur, water, and air is raised to the surface.

193. Extraction, Frasch Method. — On account of the overlying beds of quicksands, several companies failed to extract the sulphur from the Louisiana deposits discovered in 1865. Finally an ingenious method was perfected by Herman Frasch.

In the Frasch process, a hole is drilled and piped down through the 500 feet of overlying deposits to the bottom of the

sulphur bed, often 200 feet more. Inside the large pipe which cases the hole for the entire distance is a 6-inch pipe, and inside this is a 3-inch pipe, which in turn surrounds a 1-inch pipe (Fig. 76). Through the 6-inch pipe, water, heated to 167° C. under pressure, is forced down the well to melt the sulphur below. Hot compressed air, coming down through the 1-inch pipe, mingles with the liquid sulphur, and produces a frothy, comparatively light liquid. This is raised to the relay stations at the surface by the air-lift action of the compressed air.

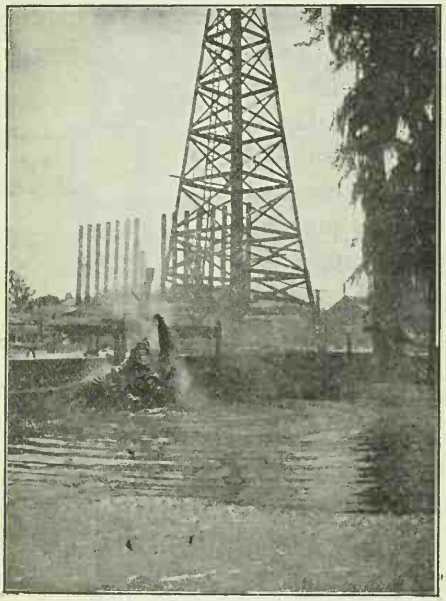


FIGURE 77.

On reaching the surface, the frothy mixture of melted sulphur, water, and air discharges into huge bins.

From the relay stations, centrifugal pumps force the melted sulphur through pipe lines into huge bins (Fig. 77) where it solidifies, forming enormous blocks of solid sulphur (Fig. 78) of remarkable purity (99%). The blocks are blasted and the broken-up sulphur loaded on cars by means of a locomotive crane and a hoist grab bucket. This process shows how a knowledge of scientific facts and principles is ingeniously applied to solve a difficult problem.

194. Forms of sulphur. — No element displays a greater variety of forms than sulphur. Four of these are well known, and are easily obtained by the following methods:

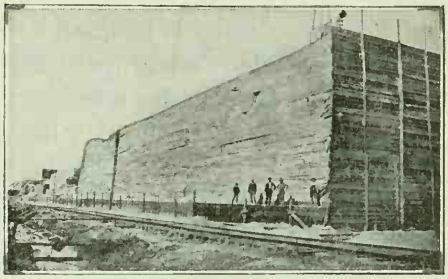


FIGURE 78.

The sulphur in this huge block was melted and forced to the surface from beds 500 feet below ground.

(1) *Crystallization from carbon disulphide.*

Ordinary roll sulphur is nearly pure rhombic sulphur. Carbon disulphide dissolves powdered roll sulphur very readily. The solvent evaporates quickly at ordinary temperatures, so that as the solution stands, the sulphur soon begins to be deposited, just as salt is deposited when a solution of it is evaporated. From its solution in carbon disulphide, the sulphur is deposited in crystals of a beautifully regular octahedral shape. This form is *rhombic* sulphur (Fig. 79). It is soluble in carbon disulphide, and has a density of 2.06.

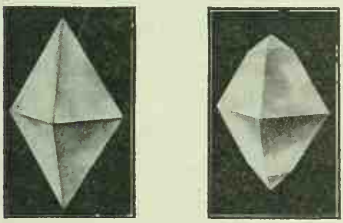


FIGURE 79.

Idealized crystals of the rhombic allotropic form of sulphur. They result from the evaporation of carbon disulphide from a solution of sulphur in this volatile liquid.

(2) *Crystallization of melted sulphur.*

Sulphur is melted at as low a temperature as possible, and then allowed to cool until crystals appear at the surface. On

pouring off the sulphur which is still liquid, the solid part is found in crystals shaped like long, narrow prisms with sharp ends (Fig. 80). This kind of sulphur is known as *prismatic* sulphur. Its density is 1.96, and it differs in other properties from the rhombic variety (page 203). The prismatic form is unstable. On standing a few hours, its crystals lose their transparency, become more brittle, and increase in density. Examination by *polarized light* shows that the long, narrow prisms have broken up into minute rhombic crystals.

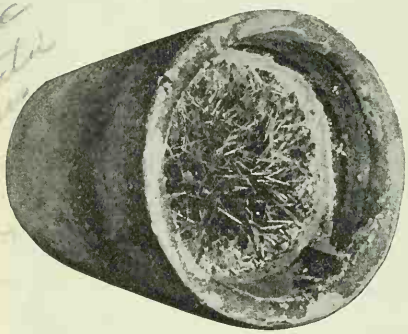


FIGURE 80.

Another allotropic form of sulphur — the prismatic, formed during the slow cooling of melted sulphur.

(3) *Sudden cooling of boiling sulphur.*

By application of considerable heat sulphur can be made to boil. Before it reaches its boiling point (445°), it goes through some interesting and unusual changes. When just above its melting point, sulphur is a mobile liquid of a light amber color. As the temperature rises, the sulphur darkens rapidly and thickens so that it can hardly be poured from the inverted test tube; on further heating, it again becomes less viscous, and finally boils, forming a pale orange-colored vapor.

When boiling sulphur is suddenly cooled by pouring into cold water, the cooled sulphur assumes a non-crystalline form (Fig. 81), is of a rubber-like consistency, and is light amber in color. Because of its lack of crystalline form it is said to be *amorphous* sulphur. This differs from the rhombic

form in being insoluble in carbon disulphide. It is sometimes spoken of as *plastic sulphur*. Like prismatic sulphur, it is unstable and is changed in the course of time into the stable rhombic form. In this change the amorphous sulphur loses its plastic character and becomes soluble in carbon disulphide.

(4) *Milk of sulphur.*

If sulphur is dissolved in some alkali, as sodium hydroxide, and hydrochloric acid is added to the solution, a white, finely divided precipitate is obtained. This precipitate is a kind of amorphous sulphur. When shaken with water it gives a fluid known as *milk of sulphur.*

FIGURE 81.

A third allotropic form of sulphur — the amorphous, which results when very hot melted sulphur is cooled suddenly by being poured into water.

195. Allotropic Forms. — These forms of sulphur, rhombic, prismatic, and amorphous, are known as *allotropic forms.* A number of other elements besides sulphur occur in several different modifications known as allotropic forms. The diamond and the graphite used in lead pencils are two of the allotropic forms of carbon. These two forms are strikingly different in physical properties, but they are the same element, carbon. Oxygen and ozone are allotropic forms of the same element.

Allotropic forms are varieties of the same element which differ in physical properties.

196. Stability of the Allotropic Forms. — At temperatures up to 96° C. all forms of sulphur tend to assume the rhombic form. From 96° to 114° the stable form is the prismatic variety. If crystals of the rhombic variety are put into a test tube and kept standing in boiling water for several days, the form will be changed to minute crystals of the prismatic variety. Thus it is seen that the form which the sulphur assumes depends on the temperature. It is generally true that each of the allotropic forms of any element is stable under certain definite conditions. By changing the conditions, allotropic forms frequently can be converted into one another.

The *commercial* forms of sulphur are flowers of sulphur and roll sulphur. *Flowers of sulphur* is formed by the sudden cooling of sulphur vapor. Flowers of sulphur is made up of the rhombic form, together with a smaller proportion of the amorphous form, as is shown by the fact that flowers of sulphur is only partly soluble in carbon disulphide. *Roll sulphur* is made by allowing melted sulphur to cool in molds. Roll sulphur consists almost entirely of the rhombic variety.

197. Chemical Properties. — All forms of sulphur burn readily when heated in the presence of oxygen; sulphur dioxide is formed as a product of the action. Sulphur is capable of taking oxygen away from compounds:

$$S + O_2 \longrightarrow SO_2$$

It does not, however, make a very satisfactory reducing agent, because it is likely to combine with the products of the reduction.

Sulphur is a moderately active element. It combines readily with many metals, often with the evolution of light and heat. In a sense, then, it may be said to support com-

bustion. This can be shown by heating sulphur in a test tube until it boils and the sulphur vapor nearly fills the tube; on placing a strip of very thin copper in the tube, it takes fire and burns, copper sulphide being formed:

$$Cu + S \longrightarrow CuS$$

Powdered zinc and sulphur, if mixed in certain proportions, will combine almost explosively when ignited, with the formation of zinc sulphide (Fig. 82):

$$Zn + S \longrightarrow ZnS$$

A mixture of iron filings and sulphur, when heated, yields ferrous sulphide:

$$Fe + S \longrightarrow FeS$$

Sulphur does not unite very readily with non-metals. Such compounds, except those with oxygen, are not very stable.

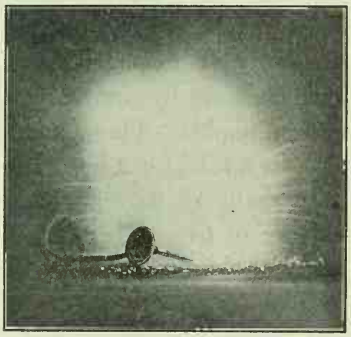


FIGURE 82.

When a mixture of zinc dust and sulphur is ignited, the two combine with explosive violence.

198. Sulphides. — The metallic sulphides form a very important class of compounds, since many metals are extracted from sulphide ores. Most of the sulphides are insoluble in water. Several of them have beautiful colors and are used as pigments in paint making. The analytical chemist also uses these compounds as a means of identifying metals.

The blackening or tarnishing of metals is sometimes due to the action of sulphur. This is particularly true of silver. Sulphur or sulphur compounds get into the air from illuminat-

ing gas or from burning coal and, acting on silver, produce the black sulphide, Ag_2S.

The tarnishing of silverware by the yolk of an egg or by mustard is due to the sulphur compounds contained in these substances. Brass and copper are also readily tarnished by sulphur and some of its compounds.

199. Resemblances of Sulphur to Other Elements. — In the ease with which it combines with other elements, particularly metals, sulphur resembles both chlorine and oxygen. Generally it displays the closer resemblance to oxygen. This is shown by comparing the solubility in water of oxides and sulphides. Those metals which form insoluble oxides also, as a rule, form insoluble sulphides.

In many of its compounds sulphur, like oxygen, has a valence of *two*. Therefore the sulphides and the oxides of many of the elements have similar formulas:

Element	Sulphide	Oxide
Copper	CuS	CuO
Zinc	ZnS	ZnO
Hydrogen	H_2S	H_2O
Lead	PbS	PbO
Mercury	HgS	HgO

The electron theory gives a clear explanation of the similarity in the chemical properties of oxygen and sulphur, just as it did in the case of the three very similar metals lithium, sodium, and potassium. The atomic number of oxygen is 8; this gives an outer ring of six electrons, two less than are needed for completeness. The atomic number of sulphur is 16; this means two electrons for the first ring, eight for a second, and leaves six for the third and outer

shell. So both oxygen and sulphur are *borrowers*, or non-metals, with a valence of two.

200. Uses of Sulphur. — Sulphur is used in making sulphur dioxide, which is employed in making sulphuric acid, the most important sulphur compound. Sulphur dioxide is also used for bleaching and disinfecting. Sulphur or some compound of sulphur serves for the hardening (vulcanizing) of rubber. Sulphur is important for the manufacture of fireworks and black gunpowder, while an increasing use is in the making of carbon disulphide. Sulphur is extensively employed as a constituent of sprays for trees, shrubs, and vines, to destroy certain insects and fungous growths.

Hydrogen Sulphide

201. Preparation. — Hydrogen sulphide, H_2S, is formed slowly and in small quantity when hydrogen is passed over heated sulphur. The presence of the gas is shown by the blackening of a strip of paper moistened with lead acetate. The difficulty of forming hydrogen sulphide by the direct union of the elements is in strong contrast to the great readiness with which the hydrogen compounds that have been studied so far, are formed. The lack of a strong tendency in hydrogen and sulphur to combine indicates the unstable character of their product.

When albumen, or other organic matter containing sulphur, decays, hydrogen sulphide is one of the substances formed. If a little sulphur is added to a fermenting sugar solution, hydrogen sulphide is produced. The characteristics of sulphur spring water are due to dissolved hydrogen sulphide.

For practical use hydrogen sulphide is readily formed by

the action of dilute hydrochloric acid on ferrous sulphide (Fig. 83):

$$FeS + 2\,HCl \longrightarrow H_2S\uparrow + FeCl_2$$

The hydrogen sulphide passes off readily as a gas; for this reason the double decomposition proceeds rapidly. Other sulphides could be used in place of the ferrous sulphide, and instead of hydrochloric acid dilute sulphuric acid might be used. The heavy gas is generally collected by displacement of air.

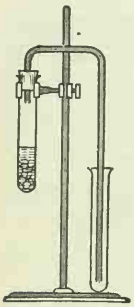


FIGURE 83. A simple apparatus for generating hydrogen sulphide in small quantities.

202. Physical Properties. — Hydrogen sulphide is a colorless gas, somewhat heavier than air, having a characteristic odor resembling rotten eggs. It dissolves to some extent in water, and therefore is not usually collected over this liquid. It is generally collected by the displacement of air. A water solution of the gas is sometimes used in the laboratory, but in such a solution the gas is decomposed in a few days by reaction with the oxygen of the air. Besides being unpleasant, the gas is injurious when inhaled, headache and sickness often resulting.

203. Chemical Properties. — If there is an ample supply of oxygen, the gas burns readily, forming water and sulphur dioxide:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

With a limited quantity of oxygen, sulphur is formed:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

The fact that a water solution of hydrogen sulphide is a poor conductor of electricity shows that as an acid it is very

weak. The solution reddens blue litmus very slowly, and the color is never as deep as that produced by solutions of strong acids.

204. Formation of Sulphides. — Hydrogen sulphide acts on most metals, forming sulphides and liberating hydrogen:

$$Pb + H_2S \longrightarrow PbS + H_2$$
$$2\,Ag + H_2S \longrightarrow Ag_2S + H_2$$

When hydrogen sulphide is passed into a solution of copper sulphate, copper sulphide is formed:

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

In ionized form:

$$Cu^{++} + SO_4^{--} + 2\,H^+ + S^{--} \longrightarrow CuS\downarrow + 2\,H^+ + SO_4^{--}$$

A similar reaction occurs with the dissolved salts of many metals, as lead, silver, and tin. In such cases the determining factor that makes the action possible is the insolubility of the metallic sulphide, either in water or in the dilute acid that is formed as a result of the action. We have seen that metallic sulphides can generally be formed in three different ways, for example:

$$2\,Ag + S \longrightarrow Ag_2S$$
$$2\,Ag + H_2S \longrightarrow Ag_2S + H_2$$
$$2\,AgNO_3 + H_2S \longrightarrow Ag_2S\downarrow + 2\,HNO_3$$

The possibility of precipitating metallic sulphides by this third method is of great value to the analytical chemist in determining the composition of unknown substances. The identification of the metal in a particular case is made by means of the color of the sulphide, its solubility in various reagents, or by other characteristic reactions.

TABLE OF CERTAIN SULPHIDES

NAME	FORMULA	COLOR	DISSOLVES IN
Mercuric sulphide	HgS	Black	Aqua regia
Copper sulphide	CuS	Black	Concentrated nitric acid
Cadmium sulphide	CdS	Yellow	Concentrated nitric acid
Arsenic sulphide	As_2S_3	Yellow	Yellow ammonium sulphide
Antimony sulphide	Sb_2S_3	Orange	Yellow ammonium sulphide
Zinc sulphide	ZnS	White	Dilute acids

SUMMARY

Sulphur is found uncombined (native), or combined in the form of sulphides and sulphates. In Texas, native sulphur is melted underground and forced to the surface.

Commercial varieties of sulphur are flowers of sulphur and lump sulphur.

Allotropic forms of an element are varieties of the same element that differ in physical properties.

Allotropic forms of sulphur are the rhombic, the prismatic, and the amorphous. The latter exists in several modifications.

	RHOMBIC SULPHUR	PRISMATIC SULPHUR	AMORPHOUS SULPHUR
Specific gravity	2.06	1.96	1.95
Solubility	Soluble in carbon disulphide	Soluble in carbon disulphide	Insoluble in carbon disulphide
Stability	Stable below 96°	Stable between 96° and 114°	Stable above 114°

Sulphur **melts** at 114° and **boils** at 445°; it is a non-conductor of electricity.

Sulphur is a **moderately active** element; it burns in air, unites directly with many elements, and resembles oxygen in its chemical action.

Sulphur is **used** for making sulphur dioxide, sulphuric acid, sulphides of metals, and carbon disulphide. Sulphur or some compound of sulphur is used in vulcanizing rubber.

Hydrogen sulphide occurs in volcanic gases and in the water of sulphur springs, and is formed in nature by the decay of organic matter containing sulphur.

Hydrogen sulphide is prepared by the action of hydrochloric acid or of sulphuric acid with ferrous sulphide.

Physical Properties: Colorless gas, poisonous, and possessing a characteristic, disgusting odor. One volume of water at 20° dissolves 3.1 volumes of hydrogen sulphide.

Chemical properties: The water solution is a weak acid and forms sulphides with most metallic ions. The gas burns in a limited supply of air to form water and sulphur, and in an excess of air to form water and sulphur dioxide.

Hydrogen sulphide is used by chemists to precipitate certain metals from solutions as sulphides.

EXERCISES

1. Explain (in the Frasch process for obtaining sulphur) the uses of (*a*) the hot water, (*b*) the hot compressed air, (*c*) the wooden bins.

2. What is meant by the *allotropic forms* of an element? Name three allotropic forms of sulphur.

3. State what allotropic form or forms of sulphur exist in each of the following commercial varieties: roll sulphur, milk of sulphur, and flowers of sulphur.

4. What conditions determine whether sulphur is to assume the prismatic or the rhombic form?

5. Why does silverware tarnish so readily in large cities?

6. Write the formulas of five sulphides and the formulas of the corresponding oxides.

7. Starting with iron, sulphur, and hydrochloric acid, give directions for the preparation of hydrogen sulphide.

8. How many grams of ferrous sulphide would be required for the preparation of five liters of hydrogen sulphide?

9. Account for the particles of sulphur found in a bottle in which a water solution of hydrogen sulphide has been standing for some days. How would the contents smell? Write the equation for the reaction that has taken place.

10. Under what conditions is sulphur obtained when hydrogen sulphide burns?

11. How many liters of oxygen would be required for the complete combustion of four liters of hydrogen sulphide?

12. Account for the fact that a water solution of hydrogen sulphide is not so active an acid as a water solution of hydrogen chloride.

13. How many grams of hydrogen sulphide would be required to combine with the copper in 0.1 gram of copper sulphate?

14. Account for the unpleasant taste of the water of sulphur springs.

15. Calculate the weight of a liter of hydrogen sulphide measured under standard conditions.

16. How could hydrogen sulphide be used to distinguish a solution of a zinc salt from a solution of a lead salt?

17. Write the equations for the burning of hydrogen sulphide (*a*) in a limited supply of oxygen; (*b*) in an ample supply of oxygen.

CHAPTER XVII

OXIDES AND ACIDS OF SULPHUR

Sulphur Dioxide

205. Commercial Preparation. — When sulphur burns in oxygen or in air, sulphur dioxide is formed:

$$S + O_2 \longrightarrow SO_2$$

The odor of burning sulphur is due to the dioxide formed. Many ores are sulphides of metals, and large quantities of sulphur dioxide are prepared by roasting such ores in air.

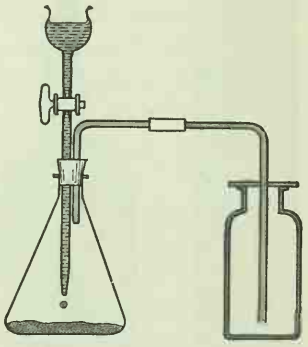


Figure 84.

Dilute sulphuric acid drops slowly on sodium acid sulphite, liberating sulphur dioxide as one of the products of the action.

206. Laboratory Preparation by Decomposition of a Sulphite. — When a mixture of sodium sulphite and dilute sulphuric acid is gently heated in a flask, sulphur dioxide is evolved, according to the equation:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

Possibly sulphurous acid is first formed, but if so, this unstable compound immediately decomposes into water and sulphur dioxide. The equations are:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SO_3$$
$$H_2SO_3 \longrightarrow H_2O + SO_2\uparrow$$
$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

The evolution of the gas may be made very regular by using sodium acid sulphite and allowing sulphuric acid (1 to 1) to fall on it, drop by drop (Fig. 84).

207. Physical Properties. — Pure sulphur dioxide is a colorless gas with a suffocating odor, and is more than twice as heavy as air.

Sulphur dioxide is one of the easiest gases to liquefy. At ordinary temperatures, a pressure of but two atmospheres is required; at the temperature of a freezing mixture of ice and salt, the ordinary atmospheric pressure is sufficient to change the gas to a liquid. Liquid sulphur dioxide is sold in glass or metal containers closed by a valve (Fig. 85).

FIGURE 85.

Two containers in which liquid sulphur dioxide comes into the market.

Sulphur dioxide is very soluble in water; one volume of water dissolves about 50 volumes of the gas at room temperature. The gas may be completely expelled from the solution by boiling.

208. Chemical Properties.— The solution of sulphur dioxide has an acid reaction and neutralizes bases, forming sulphites. Thus, with sodium hydroxide, the reaction results in the formation of sodium sulphite and water. This indicates the presence in the solution of hydrogen and sulphite ions, or, in other words, the solution

contains sulphurous acid. This acid, however, has never been separated from the solution. The acid is formed according to the equation:

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

If a solution of sulphurous acid is allowed to stand in contact with air, it very slowly takes up oxygen, forming sulphuric acid:

$$2\,H_2SO_3 + O_2 \longrightarrow 2\,H_2SO_4$$

Sulphites are likewise changed to sulphates.

209. Anhydrides. — Many oxides unite with one or more molecules of water to form new compounds. Such oxides are called *anhydrides* (meaning "without water"). An anhydride is an oxide which unites with water to form an acid or a base. Anhydrides are classified as *acid* or *basic*, according to whether they form acids or bases in combining with water. Calcium oxide, CaO, is a *basic anhydride*, as shown by the equation:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Calcium hydroxide, $Ca(OH)_2$, is a base. Since sulphur dioxide unites with water to form an acid, it is called an *acid anhydride*. An acid anhydride is named from the acid it forms when it unites with water. Hence sulphur dioxide, the anhydride of sulphurous acid, is called sulphurous anhydride.

210. Reducing Action of Sulphurous Acid. — Since sulphurous acid is readily oxidized, it acts as a reducing agent in many cases. Potassium permanganate is reduced by sulphurous acid to potassium sulphate and manganese sulphate:

$$2\,KMnO_4 + 5\,H_2SO_3 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 2\,H_2SO_4 + 3\,H_2O$$

This reducing action in the presence of water probably explains the fact that sulphur dioxide will bleach certain colors. The coloring matter is reduced, thus decolorizing the substance. In other cases, the sulphur dioxide unites directly with the coloring matter, producing a colorless compound. The color of materials bleached by sulphur dioxide will often return on exposure to the air, as in the case of straw. Bleaching by chlorine is permanent.

211. Uses. — Great quantities of sulphur dioxide or of sulphites are used in *bleaching* organic coloring matters. Paper pulp, straw, silk, wool, and other materials, which would be injured by chlorine, are decolorized by sulphur dioxide (Fig. 86). Cherries are sometimes bleached with sulphurous acid and then colored, giving them the bright shades that are seen in the canned goods of commerce.

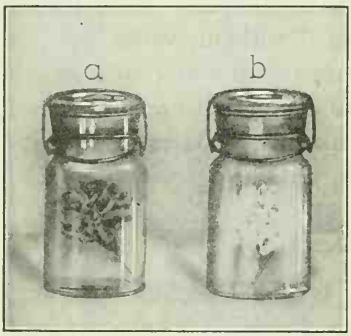


FIGURE 86.

In (*a*) the carnation is red; in (*b*) it is white. Sulphur dioxide did the bleaching.

Sulphur dioxide is sometimes used as a *disinfectant*. For this purpose, sulphur is burned, or liquid sulphur dioxide is allowed to evaporate in the room to be disinfected. In either case, the room should be tightly closed and the air in the room be kept moist, so that the disease germs may be killed by the sulphurous acid formed. This power of sulphurous acid to kill lower organisms is the reason for its use to prevent the growth of mold. A questionable use of the acid is its employment as a

food preservative. Sulphurous acid not only attacks lower organisms, but is decidedly injurious to higher forms of life.

The most important use of sulphur dioxide, however, is in the *manufacture of sulphuric acid*. Immense quantities are used for this purpose.

Sulphur Trioxide

212. Preparation. — Sulphur trioxide is prepared by the oxidation of sulphur dioxide. It is formed in very small quantities when sulphur burns. This oxidation may be made more rapid by the presence of a catalytic agent, such as finely divided platinum. Platinized asbestos is prepared by soaking asbestos in a platinum chloride solution and heating it until finely divided platinum is left on the asbestos. When a mixture of sulphur dioxide and air is passed over platinized asbestos (Fig. 87), sulphur trioxide is formed. The reaction is reversible:

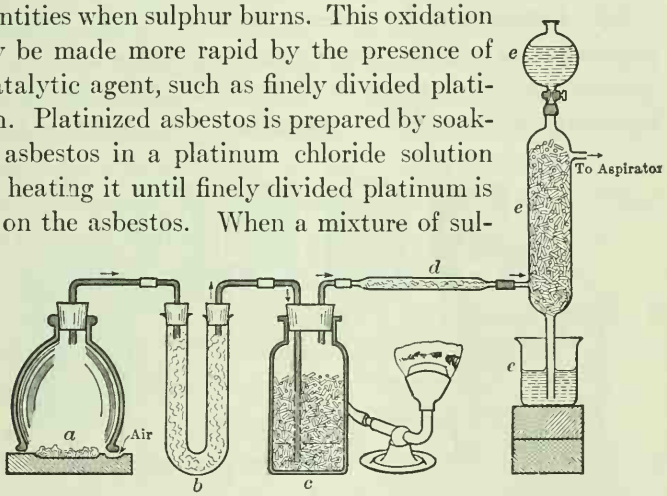


FIGURE 87.

Apparatus used in the laboratory to illustrate how sulphuric acid is manufactured on a large scale.

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$$

The temperature must be very carefully regulated, as the trioxide decomposes rapidly at a temperature slightly above that at which the best yield is obtained.

213. Solubility. — Sulphur trioxide (sulphuric anhydride) dissolves in water, forming sulphuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

As produced by the contact process, however, sulphur trioxide is more effectively dissolved by concentrated sulphuric acid. This solution is known as fuming sulphuric acid.

Sulphuric Acid

214. Preparation by Contact Process. — The *laboratory preparation* of sulphur trioxide and sulphuric acid by the contact method is represented in Figure 87. Sulphur (*a*) burns in the air which is drawn into the apparatus by an

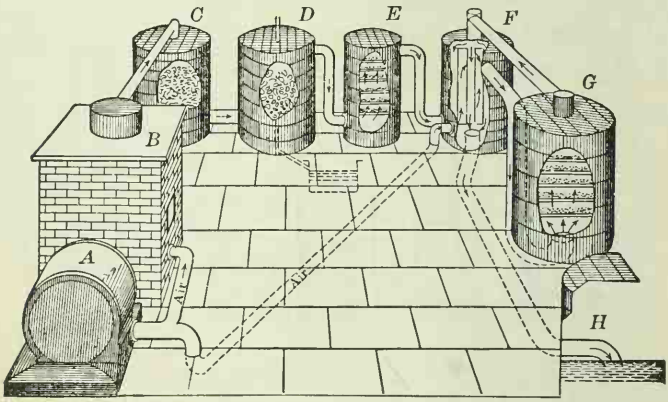


Figure 88.

Diagram of a plant used to manufacture sulphuric acid by the contact process. *A* is a blower, supplying air to *B* and *F*.

aspirator. The sulphur dioxide together with the excess of air passes into the U-tube (*b*) which is filled with some loose material to rid the gases of sulphur dust. The gases are dried in the bottle (*c*) which contains glass beads wet with concen-

trated sulphuric acid. The union of the sulphur dioxide with the oxygen of the excess air is brought about by the gently heated platinized asbestos (*d*). The sulphur trioxide resulting from the action is absorbed by concentrated sulphuric acid in the apparatus (*e*).

Pure concentrated sulphuric acid is prepared *commercially* from sulphur trioxide made by the contact process. Sulphur, or an ore containing sulphur, is burned in a furnace with air (Fig. 88, *B*). The sulphur dioxide and the other gaseous products of combustion are cooled, and freed from dust (*C*, *D*, *E*) and most of the moisture; the purified gases are then mixed with air (*F*) and passed through a chamber (*G*) containing the finely divided platinum. Unless the impurities are removed, they act on the platinum and it soon loses its catalytic power. The oxygen of the air combines with the sulphur dioxide and forms the trioxide:

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

The sulphur trioxide is passed into concentrated sulphuric acid in the tank *H* for reasons explained above, and the solution is then diluted:

$$H_2SO_4 + SO_3 \longrightarrow H_2SO_4 \cdot SO_3$$
$$H_2SO_4 \cdot SO_3 + H_2O \longrightarrow 2\,H_2SO_4$$

215. Preparation by Chamber Process. — For more than a century, all of the sulphuric acid used for commercial purposes was made by the chamber process. To-day, owing to patents on the most approved forms of apparatus for carrying on the contact process, and to the fact that manufacturers dislike to abandon expensive equipment in good working order, the chamber process is still very extensively used for the manufacture of commercial "oil of vitriol." The commercial acid produced by this process is not pure and

is not concentrated. It contains only about 60% to 70% of sulphuric acid. The advantage of the contact process over the chamber process is that the former directly produces a pure, concentrated acid.

The sulphur dioxide used in the manufacture of sulphuric acid is often obtained by burning sulphur or heating in contact with air some sulphide of a metal (Fig. 89), usually the iron sulphide, FeS_2 (pyrites). The sulphur dioxide is converted into the higher oxide by making use of nitrogen peroxide, which is obtained by the action of air with nitric oxide:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

The nitric oxide results from the reaction of nitric acid with water and sulphur dioxide. The nitric acid is made by the action of sulphuric acid with sodium nitrate:

$$2\,NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HNO_3\uparrow$$
$$2\,HNO_3 + 3\,SO_2 + 2\,H_2O \longrightarrow 3\,H_2SO_4 + 2\,NO$$

Sulphur dioxide mixed with nitrogen peroxide is passed through a tower called the Glover tower (Fig. 89), to be described later, and then into large lead chambers. Within the chambers sulphur dioxide, nitric oxide, air, and steam are brought together. Complicated reactions take place which are not well understood.

Since approximately four fifths of the air is nitrogen, it is necessary to provide for the escape of the nitrogen and at the same time prevent the escape of the oxides of nitrogen as far as possible. This is accomplished by causing the chamber gases to pass through the Gay-Lussac tower (Fig. 89). This tower is filled with coke. Sulphuric acid (78% H_2SO_4) is conveyed to the top of the tower and sprinkled on the coke. The chamber gases enter the tower at

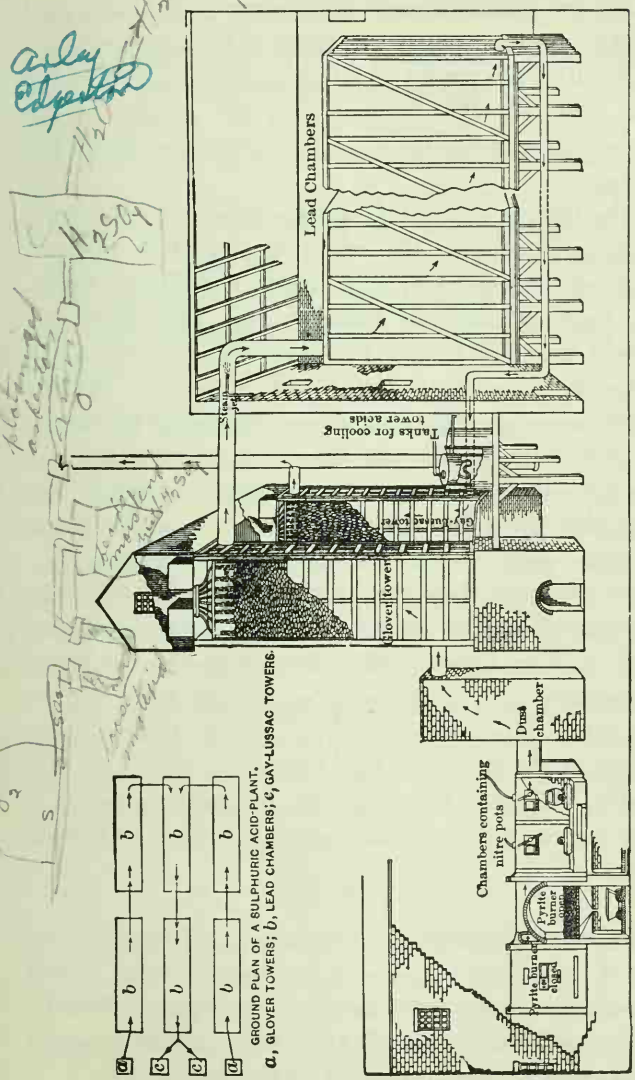


FIGURE 89.

A diagram of the chamber process for making sulphuric acid.

the bottom and ascend against the stream of sulphuric acid as it trickles down. When the plant is running properly, practically all of the oxides of nitrogen are dissolved in the sulphuric acid. In this manner they are caught in the Gay-Lussac tower, while the nitrogen, being insoluble in the acid, escapes.

From the bottom of the Gay-Lussac tower, the sulphuric acid, carrying in solution the oxides of nitrogen, is pumped to a tank on the top of another tower, the Glover tower, situated between the ore roasters and the chambers. The Glover tower is similar in construction to the Gay-Lussac tower. It is filled with lumps of quartz. At the top of the tower are two tanks, one containing the liquid coming from the Gay-Lussac tower, and the other the chamber acid (55% H_2SO_4). As a mixture of these two liquids passes down through the Glover tower, it meets the hot gases coming from the ore roasters and from the nitric acid plant, on their way to the lead chambers. The result is that the dilute chamber acid is made more concentrated, the Gay-Lussac acid is decomposed by the water in the chamber acid, and the gases are allowed to enter the chambers, while sulphuric acid (67%) is obtained from the bottom of the tower. This chamber acid can be concentrated by boiling in iron and then in platinum or silica pans, but for many commercial purposes it needs no further treatment.

216. Physical Properties. — Sulphuric acid is a heavy, oily liquid. Ordinary commercial sulphuric acid, called *oil of vitriol*, is nearly twice as heavy as water. It boils at a higher temperature (338°) than most of the common acids, and many of its uses depend on this fact.

Chemical Properties

217. Action with Water. — Sulphuric acid mixes with water in all proportions; during the mixing considerable heat is evolved. If such a mixture is to be made, *the acid should be slowly poured into the water, with constant stirring.* By doing this, the heat generated is distributed throughout the large mass of water, and the sudden generation of steam, which would cause spattering, is avoided. It is not advisable to mix sulphuric acid with water in a glass vessel, because the heat produced when the mixture is made is likely to break the glass.

218. Dehydrating Action. — Concentrated sulphuric acid absorbs moisture from the air, and this tendency of the acid to take up water explains many of its actions. Wood, paper, sugar, and similar substances, containing hydrogen and oxygen, are charred by sulphuric acid. The acid removes the hydrogen and oxygen as water, leaving a residue consisting largely of carbon. On the flesh it acts similarly, and a painful wound results.

219. Action with Metals. — With metals the acid acts in two ways. Dilute sulphuric acid does not react with all metals. If action does take place, hydrogen is evolved and metallic sulphates are formed.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$
$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2\uparrow$$

Mercury, silver, and copper are not acted on by the cold acid.

When hot concentrated acid is used, these metals react and sulphur dioxide, water, and metallic sulphates are formed.

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow$$

Thus at ordinary temperatures dilute sulphuric acid may act like hydrochloric acid, exchanging its hydrogen for metals, but when *hot and concentrated, it acts as an oxidizing agent.*

220. Action with Bases. — With bases and metallic oxides sulphuric acid reacts, forming water and sulphates:

$$2\,KOH + H_2SO_4 \longrightarrow 2\,H_2O + K_2SO_4$$
$$Ca(OH)_2 + H_2SO_4 \longrightarrow 2\,H_2O + CaSO_4$$
$$ZnO + H_2SO_4 \longrightarrow H_2O + ZnSO_4$$
$$Fe_2O_3 + 3\,H_2SO_4 \longrightarrow 3\,H_2O + Fe_2(SO_4)_3$$

221. Test for a Sulphate. — The common sulphates are all soluble except four, the sulphates of barium, strontium, calcium, and lead. In detecting the SO_4^{--} ion, a solution of barium chloride is usually employed. Representing by M^{++} any ion carrying two positive charges:

$$M^{++}SO_4^{--} + Ba^{++} + 2\,Cl^- \longrightarrow BaSO_4 \downarrow + M^{++} + 2\,Cl^-$$

The barium sulphate is easily identified, because it is white and is insoluble in water, dilute acids, and alkalies. If to the water solution of an unknown the addition of barium chloride solution produces a white precipitate which is insoluble in hydrochloric acid, the presence of sulphate ions is indicated.

222. Uses of Sulphuric Acid. — The absorption of water by sulphuric acid renders it a good dehydrating agent, and in the laboratory, gases are dried by being made to bubble through it (Fig. 26). In the manufacture of sulphuric acid by the contact process, the air and sulphur dioxide employed are dried by the use of sulphuric acid. In the purification of petroleum products, kerosene, etc., it is used to remove, by charring, materials that would give offensive

odors in burning. In the preparation of nitroglycerine, it aids the reaction by absorbing water.

As sulphuric acid has a higher boiling point than many acids, it is used in their preparation. Examples of this action have already been studied (§ 98).

On account of the conductivity of its solutions, sulphuric acid is used in electric batteries and in plating. It is used to dissolve the surface deposit on metals, previous to tinning or galvanizing. This process is called *pickling* and is essential if a firmly adherent coating is to be secured. A very important use is the conversion of certain insoluble phosphate rocks into soluble calcium phosphates, for use as fertilizers. Enormous quantities of it are used in these operations, and in hundreds of others. *There are few materials in common use by civilized man with which sulphuric acid has not been directly or indirectly connected.*

SUMMARY

Sulphur dioxide can be prepared commercially by combining oxygen with free sulphur or with sulphur in sulphides. For the laboratory, it is made by the decomposition of sulphites with acids.

The characteristic odor, the weight, and the solubility in water of sulphur dioxide are three striking **physical properties. Chemically** it is an acid anhydride, uniting with water to form sulphurous acid, which is a powerful reducing agent.

Sulphur dioxide is **used** in bleaching, as a disinfectant, as a food preservative, and, most important of all, in the manufacture of sulphuric acid.

An anhydride is an oxide that unites with water to form an acid or a base. An acid anhydride is named from the acid that it forms with water.

Sulphur trioxide is prepared by the oxidation of sulphur dioxide in the presence of a catalytic agent.

Sulphur trioxide is the **anhydride of sulphuric acid.**

Sulphuric acid may be manufactured by the "contact process," consisting of the following steps:

(1) oxidation of sulphur to the dioxide;

(2) catalytic oxidation of the sulphur dioxide to the trioxide;

(3) dissolving the trioxide in concentrated sulphuric acid;

(4) dilution of the trioxide solution.

Sulphuric acid is a heavy, oily liquid of **high boiling point.**

With metals sulphuric acid acts in two ways. At low temperatures and when dilute, hydrogen may be evolved and the sulphate of the metal formed. When hot and concentrated, it reacts as an oxidizing agent with certain metals, forming sulphur dioxide, water, and metallic sulphates. Sulphuric acid acts with bases and metallic oxides as a typical acid, forming water and sulphates.

Sulphuric acid is **used** as a dehydrating agent, in the preparation of other acids, and in a wide range of industrial applications.

All common **sulphates** are soluble in water, except those of lead, barium, strontium, and calcium. To **test for SO_4^{--} ions,** add a solution of barium chloride to the solution to be tested; a white, granular precipitate, insoluble in dilute hydrochloric acid, indicates the presence of sulphate ions.

EXERCISES

1. Which of the laboratory methods would you use for preparing *pure* sulphur dioxide? Why?

2. How many liters of sulphur dioxide would result from the reaction of 12 grams of copper with concentrated sulphuric acid?

3. What weight of sodium sulphite must be decomposed to furnish 3.5 liters sulphur dioxide?

4. What advantages has sulphur dioxide over chlorine as a bleaching agent? What disadvantage?

5. Compare the chemical reactions in chlorine and sulphur dioxide bleaching.

6. What is an acid anhydride? Name two anhydrides containing sulphur, and give their formulas.

7. Describe the manufacture of sulphuric acid by the contact process.

8. How many pounds of sulphuric acid could be manufactured theoretically from 120 pounds of pure sulphur?

9. If a bottle partly filled with concentrated sulphuric acid is left open to the air, the liquid contents increase. Explain.

10. Calculate how many grams (*a*) of silver sulphate and (*b*) of copper sulphate you could make from a dime which is 10% copper. A dime weighs 2.48 grams.

11. Explain why concentrated sulphuric acid should be poured slowly *into water* when the two liquids are mixed.

12. Account for the darkened rings formed on wood where bottles of concentrated sulphuric acid have been standing.

13. Why can either hydrochloric or sulphuric acid be used in the preparation of hydrogen sulphide? Which of these two acids must be taken for the preparation of nitric acid? Why?

14. Explain why boiling concentrated sulphuric acid produces such frightful burns.

15. Show how hot concentrated sulphuric acid acts as an oxidizing agent with metallic silver.

16. What effect would you expect if a strip of lead were placed in dilute sulphuric acid? Explain.

17. How many cubic feet of air are needed to convert 1000 cubic feet of sulphur dioxide into sulphur trioxide, if 60% of the oxygen in the air is used?

18. Why is the civilization of a country said to be indicated by the amount of sulphuric acid it uses?

19. What is oil of vitriol? A dehydrating agent? What is meant by pickling a metal?

20. What chemical tests would you make to find out whether a given solution contains a sulphate of sodium?

CHAPTER XVIII

FORMULAS AND THEIR CALCULATION

223. What the Formula Means. — The molecule of hydrogen chloride was found to consist of one atom of hydrogen and one atom of chlorine. Its formula, therefore, is HCl. This means:

(1) one molecule of hydrogen chloride;

(2) that one hydrogen chloride molecule contains one atom of hydrogen combined with one atom of chlorine;

(3) that one hydrogen chloride molecule contains one part by weight of hydrogen and 35.5 parts by weight of chlorine;

(4) 36.5 parts of hydrogen chloride by weight;

(5) one part by volume of hydrogen chloride.

Thus, NaCl shows that in sodium chloride there is one atom of sodium for each atom of chlorine; that is, 23 parts by weight of sodium with 35.5 parts by weight of chlorine give a total of 58.5 parts of sodium chloride. NaCl would also represent one volume of the gaseous salt, but *not* of the solid salt, because only when the substance is a gas does the formula represent one part by volume.

Item 5 is very useful in chemical calculations to determine volumes of gases concerned in chemical action, but note that it applies only to gases.

224. Formulas are Determined by Analysis. — While the rules of valence are useful mechanical aids in writing formulas, the formulas so obtained are never considered re-

liable or true until they have been verified by quantitative analyses and other experimentation now to be described. In many cases, the formula we might calculate by rules of valence would prove to be wrong. Hence, while students learn to write formulas of compounds through a knowledge of valence, the real authority for their use depends, as everything in science must depend, upon carefully ascertained facts.

225. How a Formula is Determined. — (I) *If the substance is a gas or can be easily vaporized,* we can calculate the formula after we have determined by experiment (*a*) its percentage composition, and (*b*) the vapor density of the gas; (*c*) the atomic weights of the elements must also be known.

Example: Gaseous alcohol is 23 times as heavy as hydrogen. The composition of alcohol is: carbon, 52.17%; hydrogen, 13.04%; oxygen, 34.78%. The atomic weights are 12, 1, and 16 respectively. Calculate the formula of alcohol.

Solution: Since alcohol in the form of a gas is 23 times as heavy as hydrogen, the molecular weight must be 46 (§ 115). This follows because the formula of hydrogen is H_2 (§ 112), and from Avogadro's Hypothesis (§ 111).

The weight of the carbon in each molecule is 52.17% of 46, or 24. Since each atom of carbon weighs 12, there must be 2 carbon atoms in each alcohol molecule to make up the 24 parts of carbon.

The weight of the hydrogen in the alcohol molecule is 13.04% of 46, which is 6. As each hydrogen atom weighs 1, there must be 6 hydrogen atoms in the alcohol molecule.

The oxygen of the alcohol molecule is 34.78% of 46, which is 16. Each oxygen atom weighs 16, so there is one oxygen atom in the alcohol molecule.

The formula of alcohol is therefore, C_2H_6O.

Whenever the density of the compound in the gaseous state can be determined, the formula can be calculated by this method.

Example: Acetylene is 13 times as dense as hydrogen; its composition is carbon, 92.3%; hydrogen, 7.7%. What is its formula?

Solution: Since the acetylene is 13 times as heavy as hydrogen, its molecular weight is 26.

	Percentage Composition	Weight of Element in Molecule	Atomic Weight	Number of Atoms
Carbon . . .	92.3	24	12	2
Hydrogen . .	7.7	2	1	2

Hence the formula of acetylene is C_2H_2.

(II) *When a compound cannot be obtained as a gas,* we generally calculate the simplest formula that will agree with the composition by weight.

Example: The percentage composition of sulphuric acid is hydrogen, 2.04%; sulphur, 32.65%; oxygen, 65.31%. What is the formula?

Solution: If we divide the parts by weight of each of these elements by its atomic weight, we shall obtain the *relative numbers* of the atoms in the compound:

hydrogen	$2.04 \div 1 = 2.04$
sulphur	$32.65 \div 32 = 1.02$
oxygen	$65.31 \div 16 = 4.08$

For every 2.04 atoms of hydrogen, sulphuric acid must contain 1.02 atoms of sulphur and 4.08 atoms of oxygen. But

this ratio 2.04 : 1.02 : 4.08 must be reduced to small whole numbers, if we are to have the simplest formula corresponding to the composition of sulphuric acid and avoid fractional parts of atoms. In this case, these whole numbers may be found by dividing each term by the smallest term.

hydrogen $2.04 \div 1.02 = 2$
sulphur $1.02 \div 1.02 = 1$
oxygen $4.08 \div 1.02 = 4$

H_2SO_4 is, therefore, the simplest formula that can represent the composition of sulphuric acid.

Whenever the molecular weight cannot be determined, the simplest formula that agrees with the composition by weight is the one that is used.

Example: The composition of magnetite is iron, 72.41%; oxygen, 27.59%. What is the simplest formula?

Solution:

	Weight	Atomic Weight	Atomic Ratio	Simplest Ratio
Iron	72.41	56	1.29	3
Oxygen . . .	27.59	16	1.72	4

The formula of magnetite is therefore Fe_3O_4. In this reduction of the atomic ratio to whole numbers the greatest common divisor, 0.43, was used.

226. How Percentage Composition is Found from the Formula. — If the formula of a compound is known, the percentage composition can be calculated.

Example: The formula of ferric oxide is Fe_2O_3; the atomic weight of iron is 56, of oxygen 16. Find the percentage composition.

The formula Fe_2O_3 represents:

2×56, or 112 parts by weight of iron, and
3×16, or 48 parts by weight of oxygen, making
160 parts by weight of ferric oxide.

$\frac{112}{160}$, that is, 70% by weight, is iron, and

$\frac{48}{160}$, that is, 30% by weight, is oxygen.

The percentage composition is of use in determining what actual weight of an element is present in a given weight of a compound. Thus, in 2000 lbs. of ferric oxide (Fe_2O_3) there is 70% iron. This is 1400 lbs.

SUMMARY

The formula of a gas is calculated from the density of the gas and its percentage composition. The formula of a gas represents an actual molecule. Coefficients of gases in chemical equations indicate relative volumes.

The formula of a non-volatile substance is calculated from its percentage composition.

The percentage of any element in a compound can be calculated from the formula of the compound.

EXERCISES

1. Define and illustrate (*a*) a symbol; (*b*) a chemical formula.

2. State the meaning of each symbol and figure in each of the following formulas:

HCl; H_2SO_4; CO_2; $Ca(NO_3)_2$; C_2H_6O.

3. How many atoms of hydrogen in each of the following:

HBr; NH_3; $NH_4C_2H_3O_2$; $(NH_4)Al(SO_4)_2$?

4. Making use of the table of atomic weights on the back cover, calculate the weights represented by each of the following formulas:

$$CuO;\ H_2SO_4;\ KClO_3;\ ZnCl_2;\ NaOH.$$

5. How many times as heavy as hydrogen is each of the following gases:

$$O_2;\ O_3;\ HCl;\ CO_2;\ NH_3?$$

6. If a liter of hydrogen weighs 0.09 gram, what will a liter of each of the following gases weigh:

$$CO_2;\ NH_3;\ SO_2;\ CO?$$

7. A certain gas is 14 times as heavy as hydrogen. What is the molecular weight of this gas? It is composed of carbon, 42.869%, and oxygen, 57.131. What is its formula? Its name?

8. The composition of ammonia, by weight, is: nitrogen, 82.35%; hydrogen, 17.65%. It is 8.5 times as heavy as hydrogen. What is its formula?

9. A substance has the composition: sulphur, 50%; oxygen, 50%. It is 32 times as dense as hydrogen. What is its formula? What is its name?

10. Methane is 8 times as heavy as hydrogen. It is 75% carbon, and 25% hydrogen. What is its formula?

11. Ethane is 15 times as dense as hydrogen. By weight, it is four fifths carbon and one fifth hydrogen. What is its formula?

12. Propane is 22 times as heavy as hydrogen. Its composition is carbon, 81.81%; hydrogen, 18.18%. What is its formula?

13. Butane is 29 times as dense as hydrogen. It is composed of carbon, 82.75%; hydrogen, 17.24%. What is its formula?

14. Calculate the simplest formula for a compound containing calcium, 29.41%; oxygen, 47.06%; and sulphur, 23.53%.

15. A hundred grams of a compound contain 30.43 grams of nitrogen and 69.57 grams of oxygen. What is the ratio between

the number of nitrogen atoms and the number of oxygen atoms? What is the simplest formula that could express the composition of this compound?

16. A substance was found to contain carbon, 40%; hydrogen, 6.67%; and oxygen, 53.33%. What is the simplest formula that would represent such a substance?

17. Marble contains 40% calcium, 12% carbon, and 48% oxygen. What formula would represent this?

18. What would be the simplest formula for a compound containing sulphur, 40%; oxygen, 60%?

19. Calculate the formula for a substance composed of carbon, 37.5%; hydrogen, 12.5%; and oxygen, 50%.

20. A solid contains sodium, 39.31%; chlorine, 60.68%. What is its empirical (simplest) formula?

21. What would be the simplest formula to represent a material containing sodium, 22.77%; boron, 21.78%; and oxygen, 55.44%?

22. What per cent of potassium chlorate, $KClO_3$, is oxygen?

23. What per cent of pyrite, FeS_2, is sulphur?

24. What per cent of water is hydrogen?

25. What is the percentage composition of CuO?

26. What is the percentage composition of common salt?

27. How much lime, CaO, could be obtained from 100 pounds of limestone, $CaCO_3$?

28. What per cent of sugar, $C_{12}H_{22}O_{11}$, is carbon?

29. What part, by weight, of ferrous oxide, FeO, is iron?

30. What part, by weight, of H_2SO_4, is the hydrogen?

31. What is the percentage composition of magnesium oxide, MgO?

CHAPTER XIX

NITROGEN AND THE ATMOSPHERE

227. Occurrence of Nitrogen. — Nitrogen has already been mentioned as constituting a large portion (nearly four fifths) of the atmosphere. It is found in a few mineral compounds, most of which, however, are the result of the activity of animal and vegetable organisms. Nitrogenous organic compounds exist in great variety; and one class, the proteins, of which the white of egg is an example, is directly concerned with life processes. In fact, nitrogen is perhaps the most characteristic element in living organisms, since protein makes up the living matter of the muscles and the protoplasm of the cells. Life without nitrogen would be impossible.

228. Preparation. — Nitrogen may be prepared from air by causing the oxygen to combine with phosphorus in the presence of water. Phosphorus is employed because its great tendency to combine with oxygen insures the completeness of the reaction, even at ordinary temperatures, and because its oxides have a great tendency to combine with water and so are rapidly removed from the gas.

Other reducing agents may be used, provided the oxide formed is easily separated from the nitrogen. If air is passed through a strongly heated tube containing fine meshed copper gauze, nearly pure nitrogen results (Fig. 90).

The reason for the use of copper is that its oxide is a non-volatile solid.

The nitrogen thus prepared always contains argon and other impurities.

Pure nitrogen can be prepared by heating ammonium nitrite, which decomposes into water and nitrogen. Owing

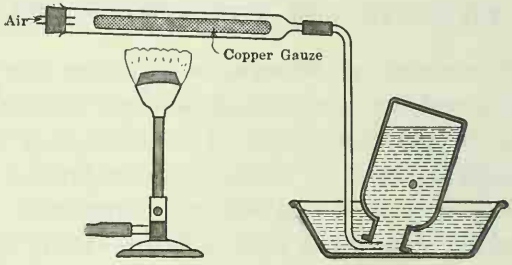


FIGURE 90.

Showing how oxygen can be removed from air by passing it over heated copper.

to the unstable nature of ammonium nitrite, a mixture of ammonium chloride and sodium nitrite is used:

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + NH_4NO_2$$

$$NH_4NO_2 \longrightarrow N_2 \uparrow + 2\,H_2O$$

$$NH_4Cl + NaNO_2 \longrightarrow N_2 \uparrow + 2\,H_2O + NaCl$$

229. Physical Properties. — Nitrogen is slightly lighter than air. It is without color, odor, or taste. Nitrogen is less soluble in water than is oxygen, so that the bubbles of gas given off, when ordinary water is warmed, contain a smaller proportion of nitrogen than air does. Cooled to a very low temperature under pressure, nitrogen becomes a colorless liquid. On further cooling, the liquid nitrogen freezes to a white solid. The liquefaction of air is used commercially

in the preparation of both oxygen and nitrogen from the air. The nitrogen of liquid air boils off before the oxygen, because the nitrogen has a lower boiling point.

Chemical Properties

230. Inactivity. — The large amount of nitrogen in the air is due to its inertness. Nitrogen does not combine readily with many substances, and its compounds are easily decomposed. The bulbs of some incandescent lamps contain nitrogen. It unites directly with few elements and with these only at high temperatures; sometimes the electric spark is necessary to cause combination. The ease and the violence with which its compounds decompose are well illustrated by nitroglycerine and guncotton.

While nitrogen does not react readily, many reactions are affected by its presence. Thus burning cannot be so vigorous in air as in oxygen, since the large proportion of nitrogen dilutes the oxygen, preventing a rapid contact with the combustible material. Moreover, heat is required to raise the temperature of the nitrogen, so that the temperature of combustion is lower than it would be if nitrogen were absent.

231. Action with Oxygen. — Nitrogen may be caused to combine slowly with oxygen by passing electric sparks through the mixture. Nitrogen will not burn in oxygen without a continual supply of external energy, as the temperature produced by the combustion is lower than the kindling point of nitrogen.

232. Action with Hydrogen. — Ammonia (NH_3) can be formed by the passage of sparks through a mixture of

hydrogen and nitrogen, or by employing a catalytic agent (§ 244). In this case, as in the similar production of the oxide, the ammonia must be removed as formed, since the reaction is reversible and a point of equilibrium is reached at which it proceeds as rapidly in one direction as in the other:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

Air

233. Composition of the Air. — The average proportions of the chief constituents of the air are as follows:

	Composition	
	By volume	By weight
Nitrogen	78.02	75.46
Oxygen	21.00	23.19
Argon	0.93	1.30
Carbon dioxide . .	0.04	0.05

Traces of other substances are often present, but under the term *air* we usually include only the nitrogen, oxygen, and argon. The relative amounts of these are practically constant, except in certain localities, as in cities, and in poorly ventilated places.

The molecular motion of the gases and the winds suffice to keep the gases of the atmosphere practically constant. Local conditions may slightly affect the composition, especially in ill-ventilated places, but even a large city produces scarcely any noticeable effect on the composition, because the total quantity of the air is so great. Fifteen pounds of air rests on each square inch of the earth, or over a ton per square foot.

234. Air is a Mixture. — Air was once regarded as an element; even now it is customary to refer to it as a single

substance. Air differs from a compound in several important particulars, as may be seen from the consideration of its oxygen and nitrogen content.

(1) If air is cooled under pressure, it is found that the oxygen liquefies before the nitrogen, and, conversely, if the liquid air is allowed to evaporate, the nitrogen vaporizes more rapidly than the oxygen. If air were a compound, it would have a definite boiling point, at which it would vaporize unchanged.

(2) If air is allowed to pass through a long unglazed porcelain tube, it is found that the lighter nitrogen passes through the porcelain walls more rapidly than the oxygen; were they combined in molecules of a compound, they would go through with equal velocities.

(3) When air is brought in contact with water, nitrogen and oxygen dissolve in the proportion of 63 : 34; while in atmospheric air the proportion is about 4 : 1 by volume.

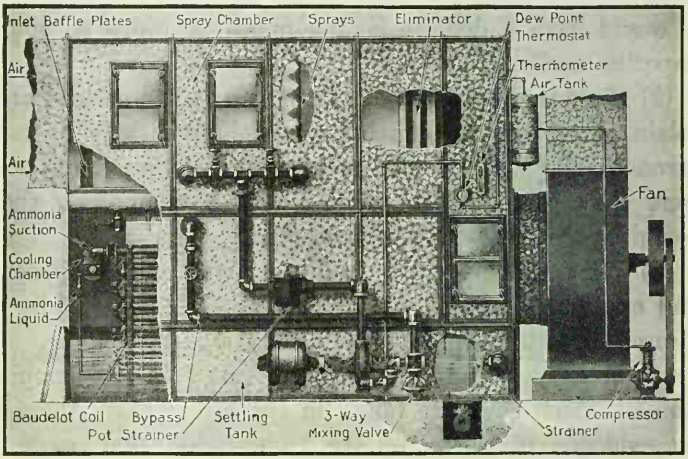
(4) If oxygen and nitrogen are mixed in the proportion in which they are found in the atmosphere, there is no evidence of reaction. We have found that when a chemical change takes place, there is usually a change in the temperature caused by the absorption or liberation of heat. Other energy changes, such as the production of light and sound (explosions), often accompany reactions. None of these energy changes occur in this case, hence there is no probability of a reaction.

(5) The composition of the air is not absolutely uniform.

235. Water Vapor of the Air. — Some water vapor, derived from evaporation, is always present in the air; the amount usually increases with the temperature; thus warm breezes blowing over bodies of water are moist. When

cooled, the vapor may condense as fog or rain. Deserts exist because the air in regions, though warm, is dry, its moisture having been lost from the cooling that occurred as the air passed over mountainous regions.

The amount of water in the air, relative to the amount necessary to saturate the air under given conditions, is



Courtesy of the Carrier Engineering Corporation.

FIGURE 91.

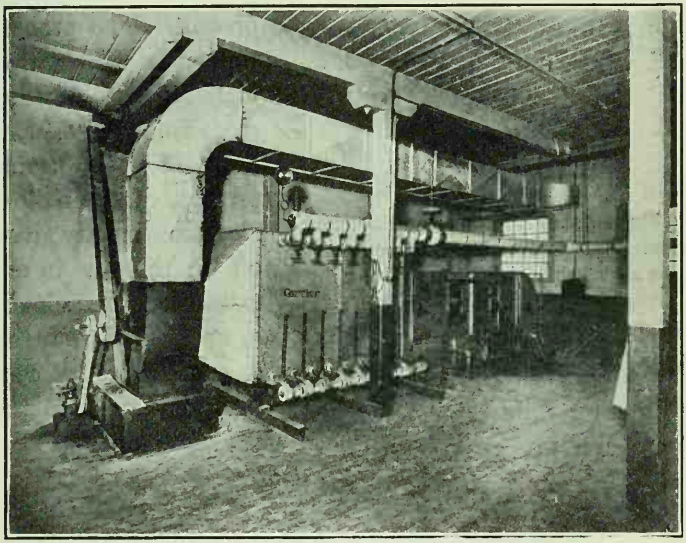
A typical air conditioning apparatus, such as is used in candy factories, showing how the air is maintained at a definite temperature and moisture content.

known as the *relative humidity*. This is high when the air is nearly saturated, and low when the air is very dry.

If the air is warm, evaporation is hastened. If, however, the air is moist, evaporation, as from the skin and lungs, is retarded and we feel oppressed and uncomfortable. If the air is dry, although warm, we note the cooling effect of the hastened evaporation. In cool

weather we are still sensible to the moisture. Only a very small amount of water vapor is required to make a crisp, bracing atmosphere become clammy and disagreeable.

When the air is a little more than half saturated, it is most comfortable. In crowded rooms it is usually too moist, and



Courtesy of the Carrier Engineering Corporation.

FIGURE 92.

Apparatus used for controlling the composition and quality of the air delivered to a factory.

unfortunately there is no simple means by which the moisture in the room can be reduced. On a large scale moisture is most readily removed by cooling and condensing the water vapor (Figs. 91, 92). Air in steam heated rooms is generally too dry for health, and various humidifiers have been devised to increase the moisture in the air of such rooms.

236. Carbon Dioxide and Nitrogen Cycles. — Carbon dioxide is always present in the air, though in a very small proportion. In normal outdoor air about 4 parts in 10,000, or four hundredths of 1%, are present. The proportion may rise rather high in a crowded room from the exhalations of the people present. Carbon dioxide is continually given off to the air in the exhalations of animals and in combustion, but as it is taken up from the air by plants, the amount in the air remains practically constant. The very small percentage of carbon dioxide in the air furnishes all the carbon needed for the growth of plants.

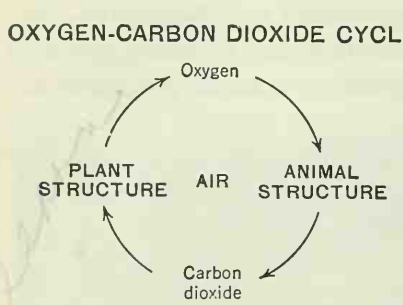


FIGURE 93.

A diagram showing how plants and animals are interdependent and how the composition of the air is kept nearly constant.

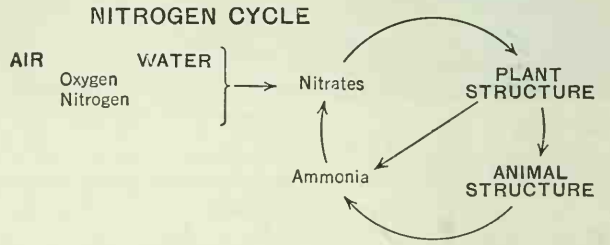


FIGURE 94.

Showing how plants and animals obtain nitrogen.

The oxygen in the air is removed by animals and replaced by plant life; thus the plant and animal life pre-

serve the balance, maintaining the atmosphere at a nearly constant composition (Figs. 93 and 95).

The nitrogen removed from the air to form soluble compounds in the soil, is taken up by plants and converted into proteins. The proteins are the source of the protoplasm of animals. The unstable proteins break up both during

Courtesy of the New York Zoölogical Society.

FIGURE 95. — A BALANCED AQUARIUM.

The fish furnish carbon dioxide to the plants, which use it and return oxygen for the fish to breathe.

the life of the plants and animals and after their death, and the nitrogen finally makes its way back to the air (Fig. 94).

237. Other Constituents of the Air. — Other materials are found in small amounts: argon, helium, and other inert gases (about 1%), traces of ammonia, sulphur compounds, and fine dust particles, which depend on local conditions and often produce climatic effects. These dust particles include a great variety of materials — steel, stone, soil,

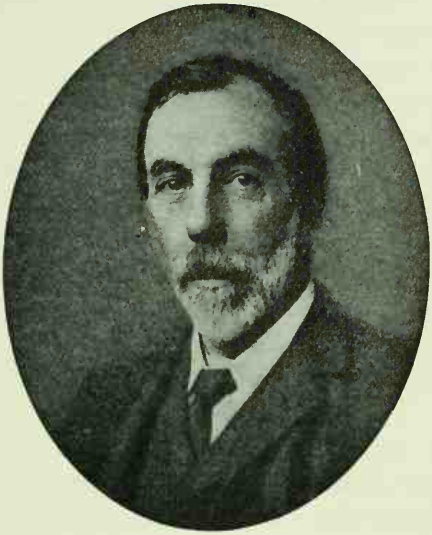
and coal dust. The organic particles include pollen grains and spores of plants, germs of disease, which are always present, shreds of various fabrics, as cotton and woolen cloth, and dried bits of refuse of all sorts.

238. Discovery of Argon. — The discovery and investigation of the inert gases in the air have afforded one of the most brilliant and interesting chapters in the history of chemistry. In 1892 Rayleigh, an English scientist, noticed that nitrogen from the air was a trifle heavier than that obtained from nitrogen compounds. This meant that the supposedly pure nitrogen from the air contained some gas, heavier than nitrogen, which had remained undetected despite the careful study of the atmosphere for more than a century.

A small amount of the hitherto unknown gas was obtained by Ramsay, an English chemist, who passed nitrogen from the air over heated magnesium which combined with the nitrogen, forming magnesium nitride, a yellowish solid. This method yielded but a trace of the new gas, and a better way was soon devised by Lord Rayleigh. Even this improved method, however, was slow, and many precautions were necessary in order to secure a very small sample of the new material.

The new substance was found to constitute about 1% of the air. It is one fourth heavier than oxygen and over one third heavier than nitrogen. All attempts to make the gas enter into chemical combination failed, and hence it was given the name *argon*, signifying *inactive*.

239. Isolation of the Other Inert Gases. — Certain irregularities in the properties of argon led Rayleigh and Ram-



Sir William Ramsay was born in Glasgow, Scotland, in 1852. He was known as a remarkably skillful experimenter. He shared with Rayleigh the honor of the discovery of argon. This element, although present in the atmosphere to the extent of about one per cent, had escaped detection because of its chemical inactivity. Ramsay's other work has been to show the presence of other previously undiscovered gases in small amount in the atmosphere; to show that helium, formerly known only as a constituent of the sun, was given off by certain minerals; and to show, with Soddy, that helium is one of the decomposition products of radium. Ramsay was awarded the Nobel Prize in 1904. He died in 1916.

say to suspect that this new gas was not itself pure. By means of liquid air the argon obtained from the atmosphere was liquefied, and, at the low temperatures obtained, repeated processes of fractional evaporation and liquefaction were carried on. The argon was found to contain minute amounts of other inert gases. Two of these could be separated only by using the extremely low temperature possible with liquid hydrogen. Three of the new inert gases were given names which bring to mind the long, baffling search for them. *Neon* means new; *xenon*, stranger; and *krypton*, hidden. Besides these three gases a trace of helium was found. This element was formerly supposed to exist only in the sun.

240. Properties. — Neon, xenon, krypton, and radon (§ 574) closely resemble argon, but each was found to have its *characteristic spectrum* and all except neon have a very low but *definite boiling point*. Thus they are elements and form a very closely related group with argon. Certain considerations have led us to believe that all these elements contain but one atom to the molecule. Their inertness with respect to chemical combination explains why no compounds containing them are known, and why they were overlooked until recently.

241. Helium. — In 1869 Lockyer noticed some lines in the sun's spectrum which did not correspond with those of any element found on earth. In 1895 Ramsay, in searching for sources of argon, examined the gases given off by certain rare minerals when heated. In the case of clevite, a gas was obtained which gave a spectrum identical with that of the supposed element in the sun, and hence was given

the name *helium*. The new element has since been obtained from the waters of certain mineral springs and from natural gas. It has been found to exist in minute quantities in the atmosphere.

Helium is a very light gas, being only twice as heavy as hydrogen. Its properties resemble those of argon, and it is therefore classed with the other inert gases. Because of its lightness and non-flammability, it may prove of use in military balloons.

Recent researches have proved that helium results from the decomposition of radium, which is considered to be an element (see Chapter XXXIX).

SUMMARY

Nitrogen constitutes the larger part of the air. It is a constituent of protoplasm and of other proteins; hence it is essential to vital processes.

It is **prepared** by:

(1) removing the oxygen from the air by phosphorus; this yields nitrogen sufficiently pure for ordinary use;

(2) heating a mixture of sodium nitrite and ammonium chloride.

One liter of nitrogen weighs 1.26 grams. Its atomic weight is 14. The nitrogen molecule contains 2 atoms (N_2).

Nitrogen is generally **inert**; under electric stress it reacts slowly with oxygen and with hydrogen A few bacteria are capable of assimilating it.

Air is essentially nitrogen, oxygen, and argon, with varying amounts of water vapor, carbon dioxide, and compounds of nitrogen and sulphur.

The amount of the air is so enormous that local conditions have little or no appreciable effect on its composition. The important

factor determining the composition is the balance maintained between plant and animal life.

Air is merely a **mixture.** Air has no definite boiling point and no definite freezing point. There is no energy change on mixing its chief components.

EXERCISES

1. Why are so few mineral compounds of nitrogen found in nature?

2. Explain how nitrogen can be obtained by passing air over heated copper.

3. Write the equation for the preparation of nitrogen from sodium nitrite. Compare as to purity the nitrogen so prepared with the nitrogen obtained by passing air over heated copper.

4. Why is it difficult to make nitrogen burn in oxygen?

5. How can nitrogen be made to combine with hydrogen? Why must the product of the reaction be removed, if the combination is to continue?

6. What are some of the chemical reactions that take place in the air during a thunderstorm?

7. Name four common substances present in the air. How could you show the presence of each?

8. State the ratio by volume of the two principal constituents of the air. How may this ratio be determined? Mention in regard to one of those constituents two important functions in nature.

9. Why is not the composition of air by weight the same as the composition by volume?

10. Give two proofs that air is a mixture rather than a chemical compound. State how it could be proved by chemical means that air contains (*a*) water, (*b*) carbon dioxide.

11. What two gases are exhaled from the lungs as excretion products? Which one of them tends to make the air of a crowded room uncomfortable?

12. Name four gases always present in the air that may be removed by some natural process, and state the process.

13. From what sources are the principal constituents of the air continually derived? By what means are they removed? Why is the composition of the air so nearly constant all over the earth?

14. What change would take place if each of the following substances was left in an open vessel: (*a*) sodium, (*b*) anhydrous calcium chloride, (*c*) lime water, (*d*) crystals of washing soda, (*e*) concentrated sulphuric acid?

15. How was it shown that the material in the air, formerly known as nitrogen, was not a pure substance?

16. Name three of the rare and inert gases and state where they may be found.

17. What is the weight of air over a city lot 25×100 ft.? How much of it is oxygen?

CHAPTER XX

NITROGEN COMPOUNDS

Ammonia

242. Natural Formation. — The most important constituent of all living organisms is protoplasm, a complex substance containing nitrogen, carbon, hydrogen, oxygen, and other elements. When a plant or animal dies and decomposition sets in, the protoplasm breaks up very quickly, yielding simpler compounds. The nitrogen unites with the hydrogen to form the gas ammonia (NH_3). The characteristic odor of ammonia can often be noted in the vicinity of heaps of decomposing animal or vegetable refuse.

Commercial Preparation

243. Destructive Distillation of Soft Coal. — Ammonia, NH_3, is one of the gases produced by the destructive distillation of soft coal. Large quantities of ammonia are obtained as a by-product during the decomposition of soft coal for the manufacture of coke and illuminating gas.

244. Haber Synthetic Process. — The possibility of utilizing the free nitrogen of the atmosphere in the manufacture of ammonia has appealed to many chemists. At present, two processes for accomplishing this bid fair to become of considerable commercial importance. In the Haber process, nitrogen and hydrogen are caused to com-

bine at a suitable temperature (500°–700° C.) and pressure (50–100 atmospheres) in the presence of a catalytic agent (*e.g.* iron):

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$$

A state of equilibrium is reached when the gas mixture contains only a small per cent of ammonia. The ammonia is removed from the mixture, and the remainder, with a new mixture of hydrogen and nitrogen, is again passed through the apparatus.

245. Cyanamid Synthetic Process. — Calcium cyanamid is prepared by passing nitrogen, obtained from liquid air, over hot calcium carbide:

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The calcium cyanamid is then treated with steam under a pressure of from 6 to 8 atmospheres:

$$CaCN_2 + 3\ H_2O \longrightarrow CaCO_3 + 2\ NH_3\uparrow$$

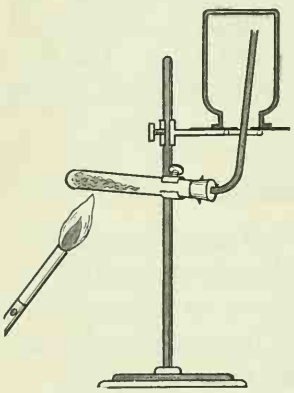


FIGURE 96.

Ammonia is generated when a mixture of ammonium sulphate and calcium hydroxide is heated.

246. Laboratory Preparation. — Ammonia is prepared in the laboratory (Fig. 96) by heating an ammonium salt with a base. Ammonium sulphate is generally used because it is the cheapest ammonium salt, and calcium hydroxide because it is the cheapest base. The reaction goes to an end because ammonium hydroxide (NH_4OH) is un-

stable and decomposes, yielding the gas ammonia (NH_3), which leaves the field of action.

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2\ NH_4OH + CaSO_4$$
$$2\ NH_4OH \longrightarrow 2\ NH_3\uparrow + 2\ H_2O$$

The reaction is usually represented by the combination of these two equations:

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2\ NH_3\uparrow + 2\ H_2O + CaSO_4$$

Ammonia can also be obtained by warming a concentrated ammonium hydroxide solution:

$$NH_4OH \longrightarrow NH_3\uparrow + H_2O$$

247. Physical Properties. — Ammonia is a colorless gas possessing a characteristic, pungent, overpowering odor. It is lighter than air, and exceedingly soluble in water. At 0° C., one volume of water will hold in solution over 1000 volumes of the gas; at ordinary temperatures about 700 volumes. This solution is known as ammonia water, or ammonium hydroxide. On being heated, or on standing exposed to air, it gives off ammonia.

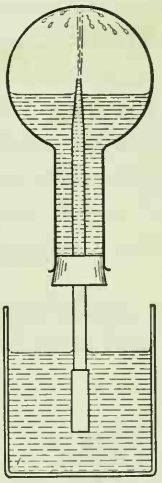


FIGURE 97.
The ammonia fountain

The great solubility of this gas is strikingly shown by the "ammonia fountain" (Fig. 97). A flask is filled with dry ammonia, and inverted over water. As soon as the ammonia comes in contact with the water, the gas rapidly dissolves and water rushes in, forming a fountain. Ammonia is easily liquefied; at ordinary temperatures a pressure of about 4.5 atmospheres is needed.

248. Chemical Properties. — Pure, dry ammonia is not an active substance; it is not readily combustible in air, but can be burned in oxygen.

The most important chemical property of ammonia is the *basic character of its water solution.* This solution, which is often incorrectly called ammonia, turns red litmus blue, neutralizes acids, and conducts electricity; it behaves like a solution of a base. We may assume, therefore, the existence of OH^- ions in the solution of ammonia. When this solution is neutralized with hydrochloric acid, a salt is formed whose composition is represented by the formula NH_4Cl. This is ammonium chloride, commonly known as *sal ammoniac.* Similar salts are formed with other acids. The group NH_4 is known as the *ammonium radical.* A water solution of ammonia, then, contains the base ammonium hydroxide, which reacts with acids to form salts:

$$NH_4OH + HCl \longrightarrow H_2O + NH_4Cl$$
$$2\ NH_4OH + H_2SO_4 \longrightarrow 2\ H_2O + (NH_4)_2SO_4$$

In the presence of moisture, ammonia combines directly with acids to form ammonium salts. For example:

$$NH_3 + HCl \longrightarrow NH_4Cl$$

In this case, the small quantity of moisture present probably combines with a little of the ammonia to form ammonium hydroxide and ionizes a part of the hydrogen chloride. When the acid is neutralized with the base, water is re-formed as one of the products of neutralization.

In the presence of a suitable catalyst (platinum heated to about 750° C.) ammonia combines with oxygen to form nitric oxide and water.

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

This is utilized as a step in the manufacture of nitric acid as explained in § 266.

249. Ammonia Water. — Ammonia water contains both ammonia and ammonium hydroxide in solution, the ammonia, water, and ammonium hydroxide being in a state of equilibrium:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

The alkaline properties of ammonia water are due to the fact that the ammonium hydroxide present dissociates, yielding hydroxyl (OH^-) ions:

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

Ammonia water is commonly kept in rubber-stoppered bottles because concentrated solutions of ammonia cause cork to disintegrate rapidly, and they attack glass so as to make it difficult to remove a glass stopper without breaking the bottle.

The value of ammonia water as a cleansing agent is due to its ability to emulsify grease and to the fact that it evaporates readily. Its basic properties give it a use in the laboratory, whenever a volatile alkali is desirable. *Household ammonia* is prepared by adding, in quantity not to exceed 6%, oleic acid to ammonia water. Cloudy ammonias contain soap and frequently other ingredients.

250. Uses of Ammonia. — The most important uses of ammonia are as a refrigerating agent and for the preparation of ammonia water. When a gas is liquefied, heat is liberated, and when the liquid returns to the gaseous state, heat is absorbed. In one process for the manufacture of

artificial ice (Fig. 98), ammonia is compressed by powerful pumps; it is then cooled and liquefied by passing cold water over the pipes containing the compressed gas. The liquid ammonia is allowed to evaporate rapidly in pipes immersed in a concentrated solution of salt or calcium chloride. The ammonia in passing from the state of a liquid to that of a gas takes heat from the salt solution and cools

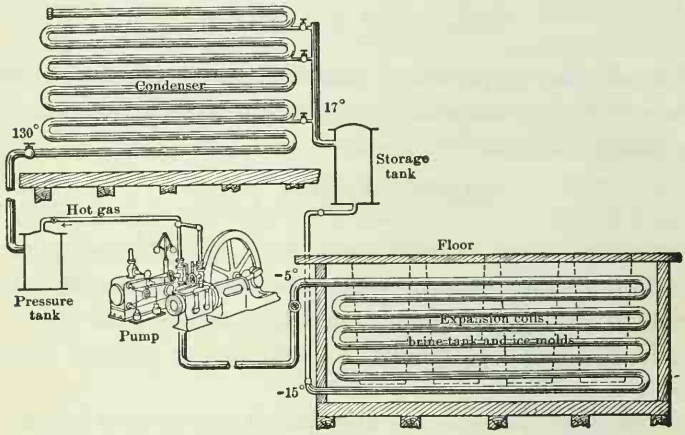


FIGURE 98.

The operation of this machine depends on the fact that liquids, in passing into the gaseous state, absorb heat.

it to a point below the freezing point of pure water. Cans of water are placed in the cold brine, and the water is frozen in from 24 to 36 hours. Cold-storage rooms may be kept cool by passing the cold brine through coils of pipe near the ceiling of the room to be cooled.

Large quantities of ammonia are used in the manufacture of sodium carbonate by the Solvay process, and in the production of ammonium salts and in the making of nitric acid (§ 266).

251. Ammonium Salts. — Although ammonium has never been obtained in a free state, there are a large number of ammonium salts.

Ammonium salts react in a manner similar to the compounds of sodium and potassium, and they may be considered as substances in which the group of atoms NH_4 (ammonium radical) plays a part like that of an atom of sodium or potassium. Thus as potassium chloride dissociates into K^+ and Cl^- ions, ammonium chloride, NH_4Cl, dissociates into NH_4^+ and Cl^- ions.

If an electric current is passed through a solution of ammonium chloride, we might expect to obtain ammonium and chlorine, since these are the ions formed. The chlorine, however, liberated at the anode reacts with the ammonium salt present in the solution, forming hydrochloric acid and nitrogen. At the cathode, the NH_4^+ ion, on discharging, decomposes into ammonia and hydrogen, the ammonia dissolving in the water.

Oxides of Nitrogen

Nitrogen combines with oxygen in five proportions, corresponding to the formulas: N_2O, nitrous oxide; NO, nitric oxide; N_2O_3, nitrous anhydride; NO_2, nitrogen peroxide; N_2O_5, nitric anhydride.

252. Nitrous Oxide. — Nitrous oxide (N_2O), laughing gas, is prepared by heating ammonium nitrate (Fig. 99);

$$NH_4NO_3 \longrightarrow N_2O\uparrow + 2\,H_2O$$

The nitrate melts and soon begins to decompose with effervescence. The heat must be carefully regulated or an explosion may occur. The nitrous oxide is a colorless

gas with a slightly sweet taste. When inhaled, it produces unconsciousness and is used for this purpose in dentistry and other minor surgical operations. In major operations, it is sometimes mixed with ether, since it lessens the bad effects of the latter anæsthetic. Nitrous oxide was the first of modern anæsthetics and was discovered by Sir Humphry Davy.

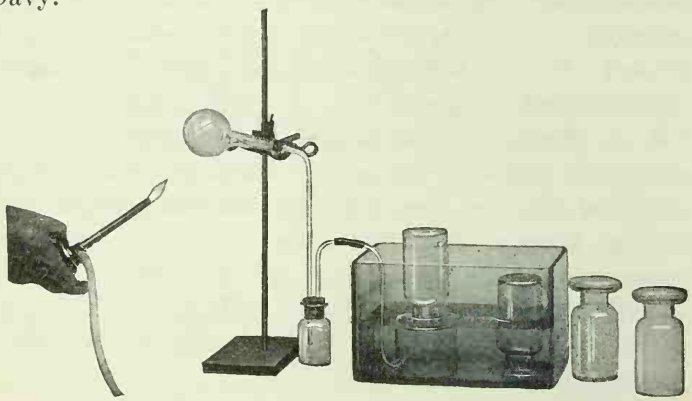


FIGURE 99.
Ammonium nitrate when heated decomposes, forming nitrous oxide and water.

Nitrous oxide supports combustion almost as well as oxygen, and is sometimes used as a substitute for it. Unlike oxygen, however, it does not react with nitric oxide, nor does it support the combustion of sulphur which is burning very feebly. It is easily liquefied, and liquid nitrous oxide is sold in small cylinders.

253. Nitric Oxide. — Nitric oxide is a colorless gas; it is generally formed during the action of dilute nitric acid with metals. In the laboratory, copper and nitric acid are used:

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow$$

Being more stable than nitrous oxide, it does not support combustion. It readily combines with oxygen, forming nitrogen peroxide, with a slight rise of temperature:

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

This action makes it useful as a catalytic agent in the chamber process for the manufacture of sulphuric acid (§ 215).

254. Nitrogen Peroxide. — Nitrogen peroxide, NO_2, is a heavy red-brown gas of disagreeable odor. It is formed immediately whenever nitric oxide is brought in contact with oxygen or with air (Fig. 100). It reacts with water, and the solution has an acid reaction. If the water is cold, the solution contains nitrous and nitric acids:

$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

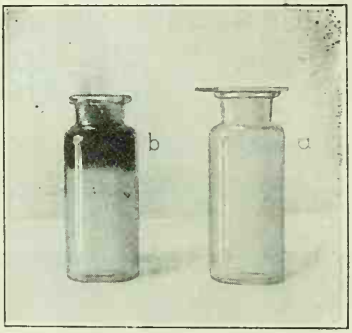


FIGURE 100.

Nitric oxide is colorless (*a*). When exposed to air (*b*), it combines with oxygen, forming nitrogen peroxide.

Thus the fumes from nitric acid, because they contain oxides of nitrogen, form nitric acid with water, and cause the corrosion usually observed on metal objects near which nitric acid is kept.

Nitrogen peroxide is readily liquefied and solidified, the liquid being yellow and the solid colorless. When the liquid vaporizes, the vapor given off at the boiling point is light brown and grows darker as the temperature rises.

Vapor density determinations indicate that vapor given off from the liquid has a composition represented by the formula N_2O_4, part of the molecules of which *immediately* dissociate into NO_2 molecules. The light-colored gas is a mixture of the two oxides. As the temperature rises, more molecules of N_2O_4 dissociate, and the dark gas at high temperatures is chiefly NO_2. These changes are represented by the equation:

$$N_2O_4 \rightleftarrows NO_2 + NO_2$$

255. Other Oxides. — Nitrogen trioxide (N_2O_3) and nitrogen pentoxide (N_2O_5) are unstable substances of no particular importance. They unite with water, forming nitrous and nitric acids:

$$H_2O + N_2O_3 \longrightarrow 2\ HNO_2$$
$$H_2O + N_2O_5 \longrightarrow 2\ HNO_3$$

Hence the trioxide is termed nitr*ous* anhydride and the pentoxide is known as nitr*ic* anhydride.

Nitric Acid

Nitric acid was known to the alchemists, who called it *aqua fortis* (strong water), because of the great chemical activity it displays. They prepared it by heating a mixture of potassium nitrate, copper sulphate, and potassium aluminum sulphate. The last two of these substances contain water of crystallization, and from this came the hydrogen which the acid contains.

256. Preparation from a Nitrate. — Both commercially and in the laboratory, nitric acid is prepared by heating a mixture of sulphuric acid and sodium nitrate (Fig. 101). The latter substance is found in large quantities in Chile.

Other nitrates might be used; but the cheapest one is selected for commercial purposes.

The reaction may proceed in two stages. The first reaction is:

$$Na^+ + NO_3^- + 2\ H^+ + SO_4^{--} \longrightarrow Na^+ + HSO_4^- + HNO_3 \uparrow$$

If there is an excess of sulphuric acid and the temperature is kept low, the reaction does not proceed beyond this point. If, on the other hand, there is an excess of sodium nitrate, the sodium hydrogen sulphate that is formed in the first action reacts at a higher temperature with more sodium nitrate, according to the equation:

$$Na^+ + NO_3^- + Na^+ + HSO_4^- \longrightarrow 2\ Na^+ + SO_4^{--} + HNO_3$$

Writing one equation to show the final results of the two stages of the reaction, we have:

$$2\ NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HNO_3 \uparrow$$

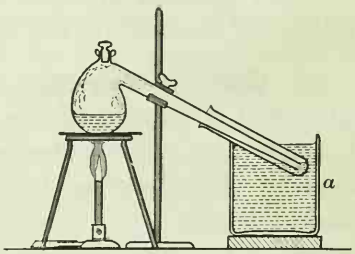


FIGURE 101.

Nitric acid is such a powerful oxidizing agent that an all-glass retort must be used when it is generated by heating sodium nitrate with concentrated sulphuric acid.

Since the second action requires a higher temperature than the first, and since nitric acid undergoes considerable decomposition at the higher temperature, it is customary to use enough sulphuric acid to give the first reaction only. Sulphuric acid is used in this operation for the reason that its boiling point is much higher than that of nitric acid. Very few acids could be substituted for sulphuric acid because most of them have too low boiling

points. In the laboratory preparation of nitric acid, the distilled acid is usually collected in a test tube or other receiver, kept cool by water in a battery jar (*a*, Fig. 101).

Nitric acid is an important article of commerce; so the reaction that has been described is carried out on a large scale. Iron retorts are used, and the acid is condensed and collected in a series of earthenware vessels.

257. Physical Properties. — Nitric acid is a colorless liquid at ordinary temperatures. The diluted acid has boiling points varying with the dilution. A mixture that contains 68% of pure nitric acid boils constantly at 120° at standard pressure.

As it is ordinarily prepared, nitric acid contains considerable water and is colored yellow by the presence of dissolved oxides of nitrogen, which result from the decomposition of the acid by the heat used in its preparation.

258. Chemical Properties. — The chemical behavior of nitric acid is very interesting. Generally its action is not a simple one. This is because it possesses two distinct chemical characteristics, both of which it displays in a marked degree.

First, it is a *very strong acid.* This is because it is highly dissociated into ions when dissolved in water, even in concentrated solution. The hydrogen ions, being present in large numbers, produce all the actions that are characteristic of acids, such as the formation of salts with bases and the transference of the electric charge of the hydrogen ion to metallic atoms, forming metallic ions, when the acid is brought in contact with a metal.

Second, nitric acid is a *powerful oxidizing agent.* This can be shown in a number of ways: charcoal can be made

to burn in nitric acid; excelsior will take fire if put into the gaseous substance; both the coloring matter and the fabric of cotton or woolen goods are quickly destroyed by it.

259. Reduction Products. — When nitric acid does oxidizing work, it is itself reduced. There are various reduction products of the acid. The product formed depends on a number of conditions, particularly on the temperature and the degree of dilution of the acid. In any case, there are several reduction products, though usually one is found in excess of the others. If the acid is moderately dilute, and acts at ordinary temperatures, the reduction product is commonly nitric oxide. From concentrated nitric acid, a large quantity of nitrogen peroxide is always obtained. From very dilute acid, the reduction product may be nitrous oxide, hydrogen, or even ammonia. Thus we see that the more dilute the acid, the farther the reduction is carried. This does not mean that the more dilute acid is the stronger oxidizing agent; on the contrary, it is because the concentrated acid is such a powerful oxidizing agent that the lower reduction products cannot escape from the acid without being themselves oxidized to a certain extent.

As we should expect from its being so strong an oxidizing agent, nitric acid is a rather unstable compound, tending to give up part of its oxygen to form more stable compounds. It will do this under the influence of light, or more readily if some oxidizable substance is present.

260. Action with Metals. — Nitric acid acts with many of the metals, but owing to its dual chemical character, it does not act on them in the same way that other acids do. Hydrogen is seldom evolved by the action of nitric acid

on metals. The gases that are given off are the reduction products of nitric acid.

The action of moderately dilute nitric acid on copper may be taken as a type of its action on the heavy metals, such as silver and mercury. Experiment shows that the chief products of this action are copper nitrate, nitric oxide, and water.

In view of the typical action of metals with acids, we might expect to get copper nitrate and hydrogen. But copper, as well as the other heavy metals, does not replace hydrogen in acids unless an oxidizing agent or something else is present to help the action. Nitric acid is a powerful oxidizing agent as well as an acid. It is able, therefore, to furnish oxygen, which combines with hydrogen to form water. What we get, therefore, would be explained if we assumed that the following reactions occur:

$$Cu + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,H$$
$$3\,H + HNO_3 \longrightarrow 2\,H_2O + NO\uparrow$$

Or perhaps the reaction might proceed thus:

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO\uparrow + 3\,O$$
$$3\,O + 6\,HNO_3 + 3\,Cu \longrightarrow 3\,H_2O + 3\,Cu(NO_3)_2$$

More convincing than either of these explanations, however, are the experimental facts expressed by the following equation:

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO\uparrow$$

Nitric acid, because of its combined acid and oxidizing character, can react with copper to form a nitrate, although this metal does not form its salts by direct action with acids that do not have oxidizing power.

The balancing of such an equation as this, involving oxidation and reduction, is a somewhat difficult matter. It will probably be found convenient to remember the numbers 3 and 8 in this reaction, and that the number of nitric oxide molecules is the same as the valence of the metal.

When concentrated nitric acid reacts with copper, nitrogen peroxide is formed in considerable quantity, as well as some nitric oxide:

$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ H_2O + 2\ NO_2 \uparrow$$

When very dilute nitric acid reacts with zinc, or metals similar to it, the nitrogen of the acid is reduced to ammonia, which then combines with more of the acid, forming ammonium nitrate:

$$4\ Zn + 10\ HNO_3 \longrightarrow 4\ Zn(NO_3)_2 + NH_4NO_3 + 3\ H_2O$$

261. Uses. — Nitric acid is used in the manufacture of all explosives such as nitroglycerine, guncotton, trinitrotoluol, ammonium nitrate, and picric acid. Large quantities of nitric acid are consumed in the manufacture of dyes, and by the nitrocellulose industries in the manufacture of such substances as collodion, celluloid and allied compounds, smokeless powders, and artificial silks. Nitric acid dissolves silver, but does not act on gold; hence it is sometimes used to separate these two metals.

Aqua regia is a mixture of nitric and hydrochloric acids. It dissolves gold and platinum. The fact that the mixture of the acids does what neither acting alone can do, is explained by the liberation of nascent chlorine by the interaction of the two acids. The hydrogen of the hydrochloric acid is oxidized by the nitric acid:

$$3\ HCl + HNO_3 \longrightarrow 3\ Cl + 2\ H_2O + NO \uparrow$$

Nitrates

262. Sodium and Potassium Nitrates. — The salts formed by the replacement of the hydrogen of nitric acid are called nitrates. The nitrates of sodium and potassium are the only ones found in nature in any considerable quantity. Potassium nitrate, ordinary saltpeter, is manufactured in a manner analogous to that by which it is produced in nature. In the presence of bases, nitrogenous organic matter decomposes under the influence of certain minute organisms called nitrifying bacteria, and has its nitrogen transformed into nitrates.

Sodium nitrate is found in large quantities in Chile, from which fact it gets the name *Chile saltpeter*. Because of its greater abundance, sodium nitrate is cheaper than potassium nitrate. The more expensive potassium nitrate is made by the reaction of sodium nitrate with potassium chloride, as explained in § 189.

One of the chief uses of potassium nitrate is for the manufacture of gunpowder. It is also used as a preservative in the making of corned beef.

263. Preparation of Nitrates. — Nitrates, like the salts of the other common acids, can be made in several simple ways in the laboratory:

(*a*) By the action of nitric acid on metals:

$$3\ Ag + 4\ HNO_3 \longrightarrow 3\ AgNO_3 + 2\ H_2O + NO\uparrow$$

As has been pointed out, hydrogen is seldom a product in the action of nitric acid on metals.

(*b*) By the action of nitric acid on oxides or hydroxides of metals:

$$ZnO + 2\ HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O$$
$$Zn(OH)_2 + 2\ HNO_3 \longrightarrow Zn(NO_3)_2 + 2\ H_2O$$

(*c*) By the action of nitric acid on salts that give a volatile product with this acid:

$$ZnCO_3 + 2\ HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O + CO_2\uparrow$$

Nitrates cannot be prepared by precipitation, because nitrates of all metals are soluble in water. This fact also prevents the use of a precipitation method as a test for a nitrate.

FIGURE 102. — TESTING FOR A NITRATE. A brown ring appears between the two layers of liquid.

264. Test for Nitrates. — The test for the NO_3 ion depends upon the oxidizing power of the NO_3 group. The substance to be tested is mixed with a solution of ferrous sulphate. Concentrated sulphuric acid is then added, so as to form a layer below the mixed solution. Nitric acid, in the presence of sulphuric acid, oxidizes ferrous sulphate to ferric sulphate and, at the same time, nitric oxide, NO, is formed as a reduction product. This combines with some of the unchanged ferrous sulphate (Fig. 102), producing a characteristic unstable compound (whose formula may be $2\ FeSO_4 \cdot NO$), which appears as a dark coloration or ring just above the heavier sulphuric acid.

All nitrates are decomposed by heat. The sodium and

potassium salts, when thus treated, give up oxygen and are converted into nitrites. Other nitrates yield oxygen and nitrogen peroxide, and the oxide of a metal.

265. Fixation of Nitrogen by Bacteria. — Certain parasitic plants of microscopic size, called nitrogen-fixing bacteria, found in the tubercles on the roots of leguminous plants, such as peas and clover (Fig. 103), have the power of taking nitrogen from the air and making it available to the plants. The nitrogen-fixing bacteria are of great importance in rendering productive soils that had remained infertile from the lack of nitrogen compounds. This is a natural *fixation of nitrogen.* The fixation of nitrogen is brought about to a small extent in nature by the passage of lightning through air. The oxygen and nitrogen unite, forming nitrogen peroxide, which in turn forms nitric acid on dissolving in water. During a thunderstorm a certain amount of nitric acid is formed in this way.

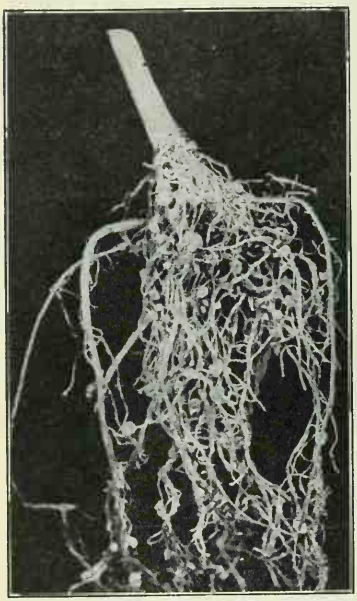


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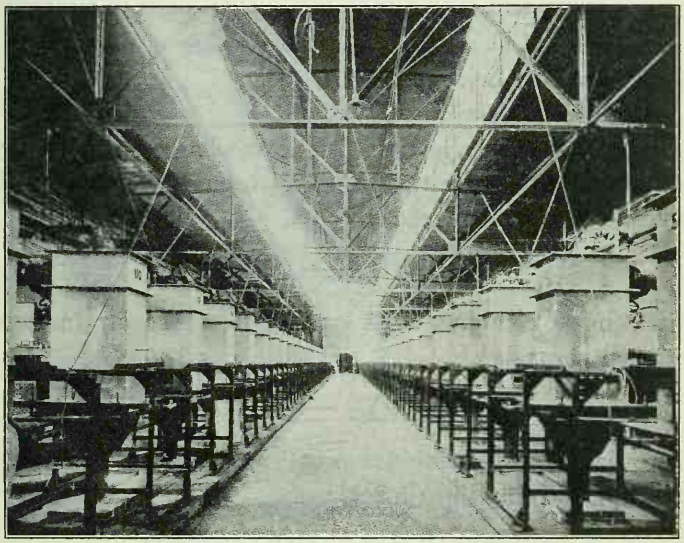
FIGURE 103.

Showing the tubercles found on the roots of leguminous plants. Nitrogen-fixing bacteria are found in these tubercles.

266. Industrial Nitrogen Fixation. — *The fixation of nitrogen is the formation of useful compounds, especially nitric*

acid, nitrates, and ammonia, by causing the free nitrogen of the air to unite with other elements. Comparatively little attention was given to this problem in the United States until German submarines infested the sea. This country then suddenly faced the possibility of being prevented from



Courtesy of the Ordnance Department of the War Department.

FIGURE 104.

A part of the great government plant at Muscle Shoals for the fixation of nitrogen. In each of these vertical tanks a mixture of ammonia and air is passing through heated platinum gauze. The ammonia is thereby converted into nitric oxide.

importing sodium nitrate from Chile. Enormous quantities of Chile saltpeter were used annually in the United States in the manufacture of agricultural fertilizers, and from sodium nitrate was made the nitric acid required for the manufacture of ammunition needed for carrying on the war. The National Defense Act of June, 1916, carried an appro-

priation of $20,000,000, placed at the disposal of the President, for the investigation of " the best, cheapest, and most available means " for the fixation of nitrogen. As a result of this act, all known processes were investigated, and when the war ended the nitrogen fixation industry was well started in this country.

Three chemical methods for the fixation of atmospheric nitrogen will be briefly outlined.

I. *The Arc Processes.*

In these processes, high tension arc discharges of electricity are passed through air, causing nitrogen to combine with oxygen to form nitric oxide:

$$N_2 + O_2 \longrightarrow 2\ NO$$

Nitric oxide combines with oxygen from the air to form nitrogen peroxide:

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

Nitrogen peroxide combines with water to form a mixture of nitrous acid and nitric acid:

$$2\ NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Nitrous acid reacts with nitrogen peroxide to form nitric acid and nitric oxide.

II. *The Cyanamide Process.*

Calcium carbide is made from coke and calcium oxide (§ 323):

$$CaO + 3\ C \longrightarrow CaC_2 + CO\uparrow$$

Calcium carbide is made to react with nitrogen to form calcium cyanamide (§ 245):

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

The calcium cyanamide can be used directly in the manufacture of agricultural fertilizers or it can be made to react with steam to form ammonia and calcium carbonate:

$$CaCN_2 + 3\ H_2O \longrightarrow 2\ NH_3\uparrow + CaCO_3$$

Ammonia in the presence of a suitable catalyst unites with oxygen to form nitric oxide and water (Fig. 104):

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

The nitric oxide combines with oxygen and water to form nitric acid as in the arc processes.

III. *Synthetic Ammonia Process.*

At a suitable temperature and pressure, in the presence of a catalyst, hydrogen can be made to combine directly with nitrogen (§ 244). The ammonia is then oxidized to nitric oxide and water, and the nitric oxide combined with oxygen and water as in the arc process.

267. Nitrification. — Nitrogen compounds are invariably found in certain tissues of both plants and animals. The nitrogen which helps to form these compounds comes from the soil, since, with one exception noted above, neither plants nor animals can take nitrogen from the air. The natural renewal of nitrates takes place slowly, and the soils become infertile because of the lack of nitrogen compounds. The difficulty is usually overcome by manuring the fields, in which case the decomposing animal matter gives up its combined nitrogen to the soil and so to growing plants. *Nitrification* is the name given to the changes that take place during the formation of nitrates by the natural processes of decay and oxidation of animal and vegetable tissues. This is brought about by nitrifying bacteria.

When enough manure is not available, nitrates or other nitrogen compounds must be added to the soil, since enormous quantities of nitrogenous farm products are consumed in cities, and most of the combined nitrogen contained in these is not returned to the soil.

268. Explosives. — Certain nitrogen compounds that contain carbon, oxygen, and hydrogen are so unstable that they decompose under the impulse of a slight shock, forming gaseous products. For this reason these compounds are powerful explosives. Nitroglycerine and guncotton are examples of this class of compounds (§ 554).

SUMMARY

Ammonia is formed in nature as a decomposition product from protoplasm.

It is **obtained commercially** as a by-product from the destructive distillation of coal or by direct combination of nitrogen and hydrogen. It may be produced by the action of a base on an ammonium salt.

Ammonia is a gas with a pungent odor; its specific gravity, relative to hydrogen, is 8.5. It is **very soluble** in water, 1 liter of water at 15° C. dissolves 720 liters of ammonia.

The **solution is basic** and contains NH_4^+ and OH^- ions It reacts with acids with the formation of water and an ammonium salt.

Ammonia is **used** as a refrigerating agent, and in the preparation of sodium bicarbonate and of **ammonia water.**

Nitrogen forms five oxides.

Nitrous oxide, N_2O, is made by heating ammonium nitrate. It is a good supporter of combustion, and is used as an anæsthetic ("laughing gas").

Nitric oxide, NO, is formed by the action of dilute nitric acid on metals. It unites with oxygen at ordinary temperatures, forming

nitrogen peroxide, NO_2. This is a brown, poisonous gas, soluble in water.

Nitrous anhydride, N_2O_3, and **nitric anhydride**, N_2O_5, are comparatively unimportant.

Nitric acid is prepared by the reaction between sulphuric acid and a nitrate.

When pure, it is a colorless liquid, with a specific gravity of 1.53.

It is a powerful **oxidizing agent.** When it reacts with metals, the hydrogen is oxidized to water and reduction products are formed. A mixture of nitric and hydrochloric acid is ***aqua regia;*** this furnishes nascent chlorine.

Nitric acid is **used** in the preparation of dyes, explosives, collodion, celluloid, and artificial silks.

The **nitrates** of sodium and potassium are the most important nitrates. Nitrates may be **prepared** by the reaction of nitric acid with:

(1) metals; (2) oxides or hydroxides; (3) salts yielding volatile products.

Potassium nitrate is **used** in gunpowder and as a meat preservative; sodium nitrate as a fertilizer and for the production of nitric acid and potassium nitrate.

Fixation of nitrogen is the conversion of the free nitrogen of the atmosphere into useful compounds.

It is brought about by the use of nitrogen-fixing bacteria and artificially by chemical methods. These are processes that are of great importance in furnishing nitrogen to plants.

Nitrifying bacteria convert organic nitrogen compounds into ammonia, nitrites, and nitrates.

Many nitrogen compounds are used in **explosives.**

EXERCISES

1. How many liters of ammonia can be obtained by the action of lime on 50 grams of ammonium chloride?

2. Why is ammonia water called the volatile alkali?

3. What method would you use to get a few cubic centimeters of ammonia gas for use in the laboratory?

4. Explain what is meant by the ammonium theory.

5. Show how the oxides of nitrogen illustrate the law of multiple proportions.

6. By what tests would you distinguish between oxygen and nitrous oxide?

7. What volume of air would convert 100 c.c. of nitric oxide, NO, into nitrogen peroxide, NO_2?

8. Compare nitric acid with sulphuric acid and with hydrochloric acid in regard to its action with metals.

9. Tell about the natural formation of (*a*) ammonia, (*b*) nitric acid, (*c*) nitrates.

10. Why is nitric acid a better solvent than hydrochloric acid for silver, mercury, and lead?

11. What is *aqua fortis? aqua regia? sal ammoniac?*

12. Upon what properties of nitric acid do most of its uses depend? Illustrate.

13. How would you test an unknown substance for the nitrate ion? For the ammonium ion?

14. Explain the significance of the statement, "No life without nitrogen."

15. State the substances and conditions necessary to yield each of the following products from certain nitrogen compounds: oxygen, hydrogen, nitric oxide, nitrogen peroxide.

16. Why has it become necessary to devote much attention to the artificial production of fertilizers containing nitrogen?

17. Describe a process for the fixation of nitrogen.

CHAPTER XXI

ELEMENTS OF THE NITROGEN GROUP

269. A Chemical Family. — Among the elements there are four that resemble nitrogen in certain ways, especially in the matter of valence. This makes a group of five elements, nitrogen, atomic weight 14, phosphorus, 31, arsenic, 75, antimony, 120, and bismuth, 208, which are spoken of as the *nitrogen family*. All of these elements form compounds in which the valence is three, and all except bismuth also have compounds in which the valence is five. All but bismuth have hydrogen compounds of the type XH_3 where X stands for the symbol of any element of the family. These four also form oxides, X_2O_3 and X_2O_5.

In properties other than valence, the members of this family show resemblances that change progressively in one direction as the atomic weight increases. Thus nitrogen is a colorless gas; phosphorus is a waxlike solid; arsenic is a dark gray solid with something of the appearance of a metal; antimony has a distinctly metallic appearance; bismuth is a metal. Similarly there is gradation of chemical properties from the non-metallic or acid-forming nitrogen and phosphorus, through the acid-forming, yet faintly metallic arsenic, to the metallic antimony and bismuth, which show but faint traces of acid character.

A *chemical family* is a group of elements which show the same valences and progressive changes in properties toward metallic character as atomic weights increase.

PHOSPHORUS

270. Occurrence. — About one fourth of the bones and teeth of animals is calcium phosphate. Rock phosphates, containing calcium phosphate, $Ca_3(PO_4)_2$, derived from the bones of prehistoric animals, are the chief source of phosphorus. Complex phosphorus compounds are a small but very essential constituent of the muscles, nerves, and brains of animals. Soluble phosphates are very necessary for plant growth, and all vegetable foods contain a small per cent of phosphorus. Man derives his largest supply from such protein foods as beans, peas, cheese, oatmeal, meat, and bread.

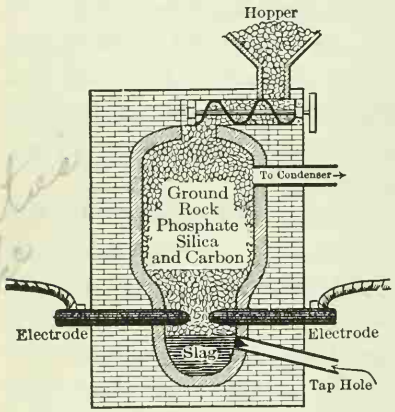


FIGURE 105.

The high temperature produced by the electrical resistance of the mixture enables the chemical reaction to proceed.

Phosphorus was discovered in 1669 by Brand, an alchemist of Hamburg, while distilling urine in the course of his attempts to find the philosopher's stone. Scheele, the Swedish chemist, prepared phosphorus from bones in 1771.

271. Preparation. — Phosphorus is obtained by heating by means of an electric current a mixture of rock phosphates, sand (SiO_2), and coke, or anthracite coal. The finely ground materials are put in the hopper of the electric furnace (Fig. 105), and then drop upon the worm conveyor which feeds them to the interior of the furnace.

The resistance of the mixture to the passage of the current between the carbon electrodes develops an intense heat which brings about the following reaction:

$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C \longrightarrow 3\ CaSiO_3 + 5\ CO\uparrow + 2\ P\uparrow$$

The calcium silicate forms a slag which collects at the bottom of the furnace, where it is tapped off from time to time. The mixture of carbon monoxide and phosphorus vapors passes out to the condenser, where the phosphorus is condensed by water, and is run into cylindrical molds.

272. White Phosphorus. — Phosphorus exists in two well-known allotropic forms — the *white* and the *red*.

White phosphorus is a waxy, translucent solid which is a little less than twice as heavy as water. It melts easily (44° C.), but on account of its inflammability, the melting must be done under water. It is readily soluble in carbon disulphide. When this solution is made to evaporate slowly, with the exclusion of air, fine and almost colorless crystals of phosphorus are obtained.

White phosphorus is a spontaneously inflammable substance. It oxidizes slowly in air, and the heat produced raises the temperature of the phosphorus to its kindling point (35° C.). For this reason, white phosphorus is kept under water. Phosphorus burns in oxygen with a brilliant flame, producing dense white fumes of phosphorus pentoxide (Fig. 7).

$$4\ P + 5\ O_2 \longrightarrow 2\ P_2O_5$$

White phosphorus when oxidizing slowly glows in the dark and some ozone is produced. The odor of the latter substance (or possibly that of an oxide of phosphorus)

has led to the common error that white phosphorus has an odor.

White phosphorus is so active that it combines readily in the cold with halogens, and at a moderate heat with sulphur and the more energetic metallic elements.

273. Red Phosphorus. — When white phosphorus is heated to about 250° C. in a vessel from which air is excluded, red phosphorus is obtained. Light brings about this conversion at ordinary temperatures. This accounts for the reddish coating that is seen on sticks of white phosphorus that have been exposed to light. The change takes place more rapidly in a carbon disulphide solution exposed to light.

The change from white to red phosphorus results in the liberation of considerable heat. This indicates that red phosphorus is the more stable form at ordinary temperatures, and that it is less active than the white. Hence red phosphorus is less easily ignited, and when burned evolves less heat than an equal weight of the white variety.

Red phosphorus is a soft, reddish powder which is slightly more than twice as heavy as water. It is insoluble not only in water, but also in carbon disulphide.

When red phosphorus is heated to about 290°, and the resulting vapors are suddenly cooled, the conversion of red to white phosphorus occurs. Thus we see that red and white phosphorus are allotropic forms comparable to those of sulphur. The red form is the stable form at all temperatures at which both forms are known, and contains less energy than the white variety. In other words, adding more energy to the red form converts it into the white variety.

274. Phosphorus Poisoning. — Red phosphorus is not poisonous, while white phosphorus is *so active a poison* that a minute quantity taken internally causes death. Formerly, in the making of matches, the workmen, by inhaling the phosphorus vapors, contracted a painful disease characterized by ulceration of the jawbones. Recently, however, legislation in this country (as is the case in practically all civilized nations of the world) has prohibited the use of poisonous white phosphorus in the manufacture of matches, and instead red phosphorus or a non-poisonous compound of phosphorus, known as phosphorus "sesquisulphide" (P_4S_3), is used.

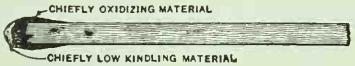


FIGURE 106.

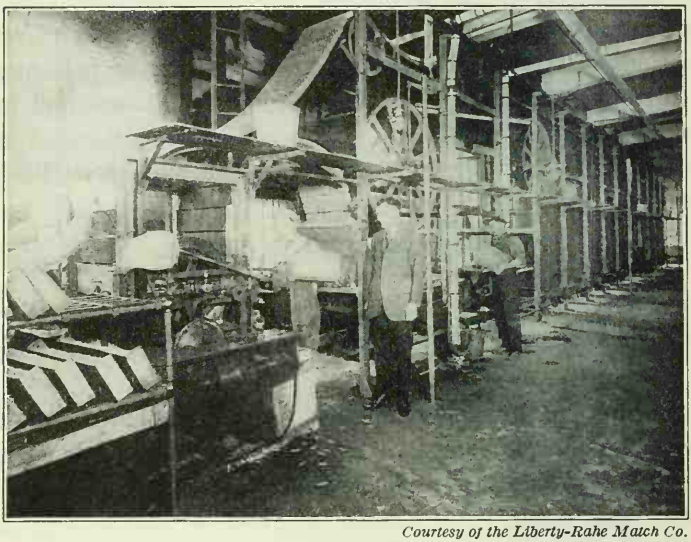
The heat produced by scratching the match ignites the tip. The oxidizing material feeds oxygen to the flame.

Because of its inflammability white phosphorus should never be handled except with tongs. Phosphorus burns are deep seated and very difficult to heal, even if suppuration does not occur. An alcohol solution of picric acid is effective in their treatment.

275. Uses. — Phosphorus is used in the manufacture of matches. *Phosphor bronze* contains from 0.2% to 4% of phosphorus, either in the form of the phosphide of copper or of the phosphide of tin. It is a hard, tenacious alloy that is not corroded by water. A minor use of phosphorus is as a constituent of poisonous pastes for rats and mice.

276. Matches. — A common *friction match* (Fig. 106) consists of a stick of soft wood, about half an inch of which has

been dipped in melted paraffin, sulphur, or other easily ignitible material; and a "head" that usually consists of two parts; one is composed chiefly of oxidizing material (such as potassium chlorate or oxide of lead), the other a "tip" that contains some low-kindling substance (such as



Courtesy of the Liberty-Rahe Match Co.

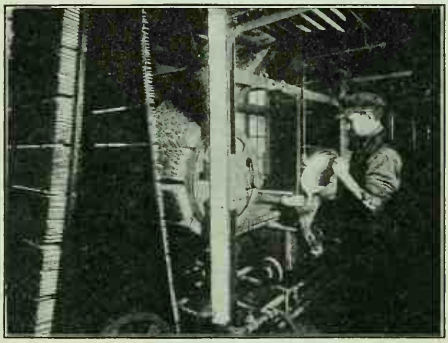
FIGURE 107.

The sticks that are to be matches are mounted like bristles in a hair brush on the belts that travel through these machines. They dip into tanks that tip them successively with paraffin, oxidizing mixture, and low kindling mixture.

phosphorus "sesquisulphide"). The tip also contains some inert material (such as ground glass or flint) to increase friction. Glue is used to make the head hold together and to make it adhere to the stick; it also serves to protect the low-kindling material from the action of the air. On rubbing, sufficient heat is generated to ignite the phosphorus

in contact with the oxidizing substance. The heat of this combustion is sufficient to ignite the paraffin, and the burning of this will in turn bring the wood to its kindling temperature.

As friction matches are always a source of fire hazard, they are often prohibited and are replaced by *safety* matches, the heads of which consist of antimony trisulphide, some oxidizing agent, such as potassium chlorate or dichromate,



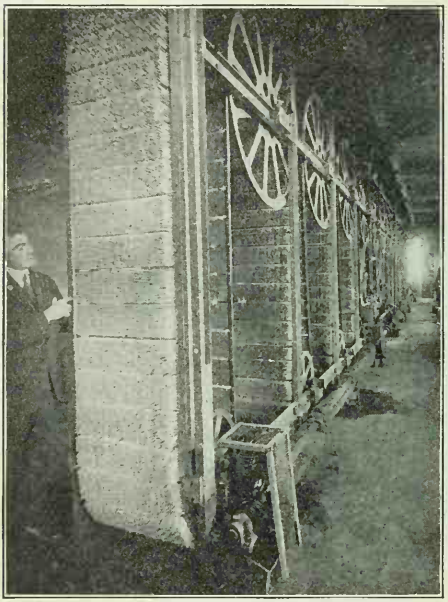
Courtesy of the Liberty-Rahe Match Co.

FIGURE 108.

The workman is pouring into the machine one of the mixtures used in putting tips on the matches.

and a little powdered glass to increase the friction, all held together with glue. The box against which they are rubbed has a surface of a thin layer of red phosphorus mixed with antimony trisulphide, manganese dioxide or other oxidizing material, and glue. Sometimes dextrin replaces the glue. As the head of the safety match is soft, it will rub off on a rough surface and not burn, but it will usually ignite on a hard, smooth surface that is a poor conductor of heat, like glass or slate blackboard.

To prevent the smoldering of glowing matches, the sticks are sometimes treated with a fireproofing material, such as a solution of ammonium phosphate. The stick is then said to be "impregnated" and is no longer a source of danger when thrown into inflammable waste material by some careless person.



Courtesy of the Liberty-Rahe Match Co.

FIGURE 109.

1,000,000 matches are being dipped and dried as they travel through this machine.

277. Compounds. — Phosphorus, like nitrogen, forms several oxides and acids. *Phosphoric oxide*, P_2O_5, is formed when phosphorus burns in a sufficient supply of air or oxygen. It is a white solid, which combines energetically with water, forming phosphoric acid, H_3PO_4. This anhydride of phosphoric acid combines so readily with water that it is used to remove the last traces of moisture in the drying of gases, and in the manufacture of certain compounds where a powerful dehydrating agent is needed.

Phosphorus oxide, P_2O_3, forms when phosphorus burns

with a limited supply of oxygen. This white solid combines with water, forming phosphorous acid, H_3PO_3.

Phosphoric acid, H_3PO_4, has several salts of common occurrence: ordinary sodium phosphate, Na_2HPO_4, used in medicine; calcium phosphate, $Ca_3(PO_4)_2$, the principal mineral constituent of the bones; monocalcium acid phosphate, $CaH_4(PO_4)_2$, used in baking powder and in fertilizers.

ARSENIC

278. Arsenic is generally found in nature combined with sulphur, associated with iron and copper. The ore is roasted, forming arsenious oxide, which is then reduced with carbon:

$$As_2O_3 + 3\ C \longrightarrow 2\ As + 3\ CO$$

279. Properties. — Arsenic is a brittle, steel-gray, crystalline solid, with a metallic luster that tarnishes rapidly in the air. It volatilizes without melting at the ordinary atmospheric pressure and has an odor like garlic. It burns with a bluish flame, forming the oxide, As_2O_3. In its physical properties arsenic resembles the metals, but in many of its chemical actions it resembles the non-metals, especially phosphorus.

280. Uses. — Arsenic is added to lead in the manufacture of shot. The melted alloy of lead and arsenic is dropped from a height through a strainer or collander into water. The arsenic lowers the melting point of the lead and makes it more fluid, so that the shot becomes spherical before cooling. The arsenic also makes the shot harder than pure lead.

281. Compounds. — *Arsenious oxide,* "white arsenic," As_2O_3, is a crystalline powder, slightly soluble in water, and, like all compounds of arsenic, is poisonous. It is used in the manufacture of certain colors, also in medicine, and as a poison. *Sulphides of arsenic,* realgar, As_2S_2, and orpiment, As_2S_3, are used as pigments. Paris green is a copper and arsenic compound used as a pigment and as an insecticide.

ANTIMONY

282. Antimony is found combined with sulphur. It is prepared in a manner analogous to that for arsenic, or by heating the sulphide with iron:

$$Sb_2S_3 + 3\ Fe \longrightarrow 2\ Sb + 3\ FeS$$

283. Properties and Uses. — Antimony is a brilliant, silver-white, crystalline, brittle solid, with a pronounced metallic luster. It does not tarnish in air, but when heated in the air burns, forming the oxide, Sb_2O_3. As it does not change in air, it is used to cover other materials, such as brass and lead alloys. When finely powdered, it is called *antimony black,* and is used to coat plaster casts in imitation of metal.

Antimony alloys are usually hard. Britannia metal and pewter contain copper, tin, lead, and antimony. Babbitt metal and other anti-friction alloys for bearings generally contain antimony. Lead contracts on solidifying; an alloy of antimony, lead, and tin expands on solidifying, and is hard. This low-melting alloy is used for type metal. The antimony compounds of commercial value are the trichloride, $SbCl_3$, "butter of antimony"; and tartar emetic, $K(SbO)C_4H_4O_6$, a soluble basic salt used in medicine.

BISMUTH

284. Properties and Uses. — Bismuth resembles antimony, but is more metallic. It has a red tinge, is brittle, crystalline, heavy, and tarnishes slowly in moist air.

Bismuth alloys are remarkable for their low melting-points. Bismuth melts at 270° C. Its two most common alloys, Wood's metal and Rose's metal, have the following composition:

	Wood's Metal	Rose's Metal
Bismuth	50.0%	48.9%
Tin	12.5%	23.6%
Cadmium	12.5%	
Lead	25.0%	27.5%
Melting points	65° C.	95° C.

Such easily melted alloys are extensively used as fuses in electric connections, in fire alarms, in safety plugs for boilers, and in automatic sprinklers in buildings. When the fusible plug of a sprinkler (Fig. 110, *a*) melts, the water rushes out from the main and strikes a cap *b*, which scatters the water in all directions. A piece of Wood's metal is sometimes placed in the gaspipe where it enters a building, so that in case of fire the alloy will melt and stop the flow of gas. Bismuth subnitrate, $Bi(OH)_2NO_3$, is a basic salt made by the hydrolysis of the normal nitrate. It is used in cosmetics, and also in certain diseases of the digestive tract.

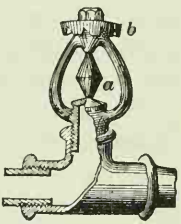


Figure 110.

If a fire starts, the fusible alloy (*a*) melts, and releases the water.

285. Comparison of the Nitrogen Group.

	Atomic Weight	Melting Point	Hydrides	Oxides	Acids
Nitrogen	14	−214°	NH_3	N_2O, NO, N_2O_3 NO_2, N_2O_5	HNO_2 HNO_3 Strong acids
Phosphorus	31	44°	PH_3	P_2O_3, P_2O_5	H_3PO_3, H_3PO_4 Weak acids
Arsenic	75	volatile	AsH_3	As_2O_3, As_2O_5	H_3AsO_3, H_3AsO_4
Antimony	120	630°	SbH_3	Sb_2O_3, Sb_2O_5	H_3SbO_4 Very weak acid
Bismuth	208	269°		Bi_2O_3	$Bi(OH)_3$, Base

SUMMARY

Phosphorus exists in allotropic forms. The common ones are the white and the red.

White phosphorus is the more active, is very inflammable and poisonous and dissolves in carbon disulphide.

Red phosphorus is not so easily ignited, is less active chemically, and does not dissolve in carbon sulphide.

Phosphorus is extracted by the heat developed by passing an electric current through a mixture of rock phosphates, sand, and coke.

Phosphorus is chiefly **used** for making matches and hard alloys.

Arsenic, though a non-metal, shows some of the characteristics of metals. It alloys with other metals and is used to make shot hard. Some of its compounds are valuable as pigments

Antimony shows the characteristics of both metals and non-metals. It is a constituent of type metal and other alloys.

Bismuth is a metal used in many fusible alloys.

EXERCISES

1. What is the per cent of phosphorus in calcium phosphate, $Ca_3(PO_4)_2$?

2. Make a sketch of the electric furnace used for extracting phosphorus. Label each part. Why must air be kept out?

3. Compare, in tabular form, white and red phosphorus with respect to (*a*) solubility in water and in carbon disulphide, (*b*) melting points, (*c*) ease of ignition, (*d*) chemical activity, (*e*) poisonous nature.

4. What weight of oxygen would be consumed in combining with 0.5 gram of phosphorus? What would be the volume of the oxygen at standard conditions?

5. Why is white phosphorus kept under water?

6. What gas may be produced during the slow oxidation of white phosphorus?

7. What weight of phosphorus would be necessary to remove the oxygen from 10 liters of air (measured at standard conditions)?

8. How may red phosphorus be changed to white? White to red?

9. Why does white phosphorus cause such bad burns?

10. State the essential differences between a safety and a friction match. How does the safety match justify its name?

11. Why do matches ignite on being rubbed?

12. Write equations to show that both phosphorus oxide and phosphoric oxide are acid anhydrides.

13. What is (*a*) phosphor bronze? (*b*) white arsenic? (*c*) type metal? (*d*) Wood's metal? (*e*) Rose's metal?

14. Describe the operation of an automatic sprinkler.

15. Reduced to standard conditions, 500 c.c. of phosphorus vapor weigh 2.79 grams. From this calculate (*a*) the vapor density, (*b*) the number of atoms in a molecule of gaseous phosphorus.

CHAPTER XXII

THE HALOGENS

The elements fluorine, chlorine, bromine, and iodine form a chemical family, known as the *halogens* (salt formers), because they unite directly with a large number of metallic elements to form salts.

Bromine

286. Occurrence. — Bromine was discovered in 1826 by Ballard, who separated it from the mother liquid of sea salt, known as *bittern* on account of the bitter taste imparted by magnesium salts. Extensive deposits of magnesium salts containing bromides are found in the almost inexhaustible salt beds at Stassfurt, Germany. The United States and Germany furnish a large percentage of all the bromine used. Large deposits of crude salt, impure sodium chloride containing bromides, occur in the states of Michigan, West Virginia, Ohio, and Kentucky. Magnesium bromide and sodium bromide are two of the substances mixed with the sodium chloride.

287. Commercial Preparation. — When the brines from the deposits mentioned above are evaporated, nearly all of the sodium chloride crystallizes out before the magnesium salts begin to separate in an appreciable quantity. The liquid remaining after a portion of the substances contained

in the original solution has crystallized, is known by the technical name of *mother liquor*. The mother liquor containing the magnesium bromide is allowed to trickle down through a tower filled with small pieces of stone or brick. Chlorine gas enters at the bottom of the tower, and, as it rises, reacts with the descending solution:

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

High pressure steam introduced into the apparatus causes the liberated bromine and any excess of chlorine to pass over at the top of the tower. The bromine is condensed in a receiver and is afterwards freed from any chlorine by redistillation.

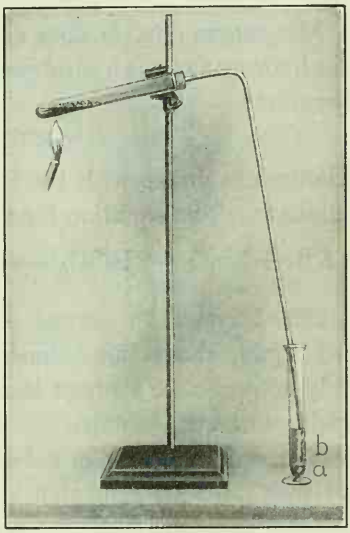


FIGURE 111.

Bromine passes into the water in the lower test tube. It is seen there partly dissolved in water (*b*), and partly as a dark red liquid forming the lower layer (*a*).

288. Laboratory Preparation. — Bromine can be prepared from the bromides by heating a mixture of a bromide, manganese dioxide, and sulphuric acid (Fig. 111), a method analogous to one of the methods described for the preparation of chlorine. Bromine, having a low boiling point, passes off in the state of vapor, which can easily be liquefied by keeping the receiver cool. If a small quantity is made, the bromine vapor can be condensed in a test tube partly filled with water (see *a* and *b* in Fig. 111).

The reaction is complex and we may think of it as taking place in three steps.

Sulphuric acid reacts with potassium bromide to produce potassium sulphate and hydrogen bromide:

$$2\ KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2\ HBr$$

Manganese dioxide acts as an oxidizing agent, oxidizing the hydrogen of the hydrobromic acid to water and liberating bromine:

$$2\ HBr + O \longrightarrow H_2O + Br_2$$

Manganese unites with the SO_4 radical, forming manganese sulphate. The equation for the complete reaction is:

$$2\,KBr + MnO_2 + 2\,H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

289. Physical Properties. — Bromine is a dark brownish red liquid, about three times as dense as water. It is the only non-metallic element that exists in the state of a liquid under ordinary conditions. Bromine has an odor somewhat resembling that of chlorine; its name is derived from a Greek word meaning stench.

Bromine vaporizes so easily that when a bottle of bromine is opened, the brownish red vapor of bromine can be seen issuing from the mouth of the bottle. If a few drops of bromine are poured into a large bottle filled with air, the vapor is seen first at the bottom of the bottle, and from here it diffuses slowly until it fills the bottle.

The vapor of bromine has a destructive action on the mucous membrane. When it comes into contact with the eyes, the irritation is sufficient to cause a copious flow of tears. Great care should be taken not to inhale bromine vapor, and never to allow the bromine to come in contact with the skin. If bromine is accidentally inhaled, the irri-

tation can be lessened by smelling of ammonia, chloroform, or alcohol. If bromine should come in contact with the skin, the injured part should be washed freely with water and then covered with a paste made by mixing sodium bicarbonate with water, or better, with some oil, as olive or cocoanut.

Bromine is somewhat soluble in water; the solution is called *bromine water*. Bromine is more soluble in aqueous solutions of the bromides than it is in pure water. It is very soluble in chloroform, in carbon tetrachloride, and in carbon disulphide. In all of these solutions it has a very characteristic orange color.

290. Chemical Properties. — The chemical behavior of bromine very closely resembles that of chlorine. Bromine is, however, not so active an element as chlorine. We have already seen that when a mixture of chlorine and hydrogen is placed in the sunlight, the elements combine with explosive violence to form hydrogen chloride. Under similar conditions, bromine vapor and hydrogen enter into only a partial combination, without any *display* of energy. Aqueous solutions of bromine bleach many dyes, but the action is not so rapid as in the case of chlorine.

Bromine combines directly with a number of elements, for example, phosphorus, antimony, copper, and iron, forming bromides.

291. Uses. — Bromine is used in the preparation of bromides and as a mild oxidizing agent in the manufacture of many organic compounds, especially certain drugs and dyes. Its water solution is used in the laboratory as an oxidizing agent.

Hydrobromic Acid

292. Preparation. — Hydrogen bromide may be prepared by the direct combination of bromine with hydrogen; this method, however, is slow and of no practical importance.

Commercially, a dilute solution of hydrobromic acid is prepared by the reaction between diluted sulphuric acid and a solution of potassium bromide. The actual carrying out of the process requires considerable time and careful regulation of temperature.

Hydrogen bromide gas cannot be prepared in a pure state by this method. When concentrated sulphuric acid is added to potassium bromide, while hydrogen bromide appears as a gas, other gases are formed at the same time. The odor of sulphur dioxide can generally be detected, and sometimes that of hydrogen sulphide. The products formed vary with the concentration of the sulphuric acid and the temperature at which the reaction takes place. The more concentrated the sulphuric acid, and the higher the temperature, the less will be the amount of the hydrogen bromide produced.

Let us consider the reactions involved when sulphur dioxide is formed. Sulphuric acid reacts with potassium bromide to form potassium sulphate and hydrogen bromide:

$$2\ KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2\ HBr\uparrow$$

The excess of concentrated sulphuric acid, however, oxidizes part of the hydrogen bromide, the result of the oxidation being water and bromine:

$$2\ HBr + H_2SO_4 \longrightarrow 2\ H_2O + SO_2\uparrow + Br_2\uparrow$$

This is similar to the action of hot concentrated sulphuric acid with copper (§ 219), in which a portion of the

sulphuric acid is reduced to sulphur dioxide, and at the same time water is formed. The fact that when one substance is oxidized some other substance is simultaneously reduced, should be constantly kept in mind.

If we use one equation to represent the formation of bromine and sulphur dioxide, by the method just considered, we obtain:

$$2\ KBr + 2\ H_2SO_4 \longrightarrow K_2SO_4 + 2\ H_2O + SO_2\uparrow + Br_2\uparrow$$

293. Properties and Uses. — Hydrogen bromide is a colorless gas, readily soluble in water, and fuming in moist air. Its solution, *hydrobromic acid*, possesses the characteristic properties of a strong acid. It is easily oxidized by the oxygen of the air, water and bromine resulting from the oxidation.

Dilute solutions of hydrobromic acid are used to some extent for medicine, and the bromides are an important series of salts.

294. Replacement of Bromine. — When chlorine is added to a solution of a bromide, free bromine appears and chlorine molecules change into chlorine ions. The solution of potassium bromide contains potassium ions, bromine ions, and molecules of potassium bromide; the undissociated and dissociated potassium bromide are in equilibrium. As soon as chlorine is added, the bromine ions give their negative charge of electricity to the chlorine molecules, which then dissociate into ions. The bromine ions, having lost their charge of electricity, unite to form bromine molecules. As soon as some of the bromine ions pass out of solution, the equilibrium between the dissociated and the undissociated potassium bromide is destroyed,

and more molecules of potassium bromide dissociate. If enough chlorine is added, all the bromine ions will finally appear as bromine molecules, and the solution will contain potassium ions, chlorine ions, molecules of potassium chloride, and molecules of bromine:

$$2\ K^+ + 2\ Br^- + Cl_2 \longrightarrow 2\ K^+ + 2\ Cl^- + Br_2$$

or

$$2\ KBr + Cl_2 \longrightarrow 2\ KCl + Br_2$$

The presence of free bromine can be shown by adding a little chloroform, carbon tetrachloride or carbon disulphide, and shaking. These liquids and water are not miscible (§ 49), and bromine is much more soluble in carbon disulphide (or chloroform) than it is in water. The bromine will be distributed between the water and the carbon disulphide in proportion to its solubility in the two liquids. The solution of bromine in carbon disulphide has a characteristic orange color; the bromine must be free, for bromine ions do not produce this characteristic color, as may be shown by shaking carbon disulphide with a solution of potassium bromide (Fig. 112, *a*). Since a small quantity of carbon disulphide can be used to remove nearly all of the free bromine from a comparatively large quantity of water by shaking, the process is called *shaking out* or *extraction.*

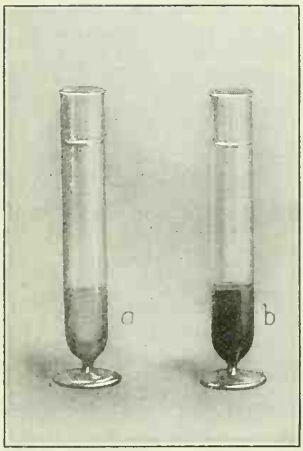


FIGURE 112.

A test for bromine. Carbon disulphide does not mix with water (*a*). It is colored orange when it is shaken with a water solution containing free bromine (*b*).

295. Test for a Bromide. — The liberation of bromine by chlorine, followed by shaking out with chloroform or carbon disulphide, is used as a test for bromine ions. If we add chlorine water to a solution of a bromide, and then shake with chloroform, the latter dissolves the free bromine, acquiring the characteristic orange coloration (Fig. 112, *b*).

Iodine

296. Discovery. — Iodine was discovered by Courtois in 1812 while he was trying to prepare potassium nitrate from liquors obtained by washing the ashes of burnt seaweed. During his experiments Courtois observed the violet color of the vapor of iodine, but the properties of the element were first carefully studied by Gay-Lussac.

297. Preparation. — When seaweed (kelp) is burned at a low temperature, the ash contains considerable quantities of the iodides of potassium and sodium. As both of these salts are readily soluble in water, they can be separated from the insoluble portion of the ash by *leaching*, that is, by allowing water to pass slowly through the ash and dissolve the soluble materials.

Iodine is obtained from potassium iodide by a process analogous to that described for the preparation of bromine (§ 288); the iodide is warmed with manganese dioxide and sulphuric acid. Iodine passes off in the form of a vapor:

$$2\,KI + MnO_2 + 2\,H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 2\,H_2O + I_2\uparrow$$

Large deposits of impure sodium nitrate are found in the dry region west of the Andes. Compounds of iodine occur in these deposits, and most of the iodine used is obtained from the mother liquor of the sodium nitrate works.

298. Physical Properties. — Iodine is a steel-gray solid (Fig. 113), very slightly soluble in water, but readily soluble in alcohol, chloroform, carbon disulphide, and aqueous solutions of potassium iodide. A solution of iodine in alcohol is called *tincture of iodine*. Solutions of iodine in chloroform and in carbon disulphide possess a characteristic violet color; iodine vapor has the same color. Iodine vaporizes slowly at ordinary temperatures. When the solid is warmed, the change takes place rapidly, and the vapor on being cooled passes directly to the state of a solid. Such a distillation of a solid is called *sublimation;* the process is used to purify some solids, *e.g.* camphor and naphthalene, in the same way as distillation is used to purify liquids.

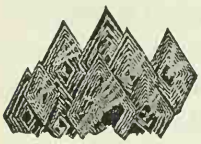


FIGURE 113.
CRYSTALS OF IODINE.

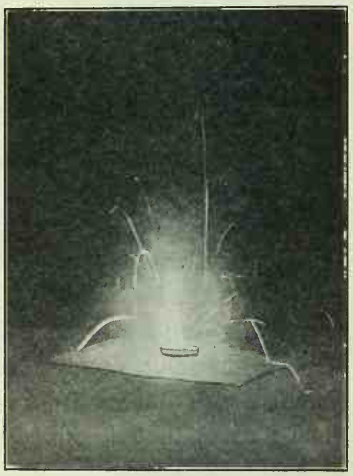


FIGURE 114.
Iodine combines vigorously with phosphorus.

299. Chemical Properties. — Iodine unites directly with many elements to form iodides. The reactions are not so energetic as in the case of either chlorine or bromine. When a piece of yellow phosphorus and a piece of iodine are brought together, they combine vigorously without the application of heat, forming phosphorus triodide, PI_3 (Fig. 114). Iodine and iron unite when heated.

300. Tests for Iodine and Iodides. — When a dilute solution of iodine is mixed with a dilute solution of starch paste, a characteristic blue color is produced. The reaction is employed in testing for either iodine or starch.

The characteristic violet color of its carbon disulphide solution affords another test for free iodine. In testing for an iodide, chlorine water is first added to liberate the iodine. Carbon disulphide is then added to the mixture and the whole is shaken. The iodine dissolves chiefly in the carbon disulphide and gives the characteristic violet color:

$$2\ KI + Cl_2 \longrightarrow 2\ KCl + I_2$$

301. Uses. — Iodine compounds are used in medicine, in photography, and for dyeing. Tincture of iodine is used for reducing swellings and is the most important household antiseptic for cuts and abrasions of the skin.

302. Preparation of Hydriodic Acid. — If concentrated sulphuric acid is added to an iodide, the odor of hydrogen sulphide is very noticeable. More hydrogen sulphide is produced than is formed when sulphuric acid is added to a bromide. This means that hydriodic acid is more easily oxidized (or is a better reducing agent) than hydrobromic acid. Sulphur dioxide and sulphur are often present as reduction products.

The action of sulphuric acid with potassium iodide can be partly represented by the following equations:

$$8\ KI + 4\ H_2SO_4 \longrightarrow 4\ K_2SO_4 + 8\ HI\uparrow$$

$$H_2SO_4 + 8\ HI \longrightarrow H_2S\uparrow + 4\ H_2O + 8\ I\uparrow$$

The equation for the complete reaction is:

$$8\ KI + 5\ H_2SO_4 \longrightarrow 4\ K_2SO_4 + 4\ H_2O + H_2S\uparrow + 8\ I\uparrow$$

Pure hydriodic acid can be readily prepared by the reaction of water with iodine and red phosphorus:

$$P + 3\ I \longrightarrow PI_3$$
$$PI_3 + 3\ H_2O \longrightarrow H_3PO_3 + 3\ HI\uparrow$$

303. Iodides. — The iodides are important compounds, finding extensive use in medicine. They are less stable than the corresponding chlorides and bromides, as is shown by the fact that either chlorine or bromine liberates iodine from the iodides:

$$2\ KI + Cl_2 \longrightarrow 2\ KCl + I_2$$
$$2\ KI + Br_2 \longrightarrow 2\ KBr + I_2$$

The presence of free iodine can be determined by the starch test or by shaking out with chloroform or with carbon disulphide.

The Halogens as a Group

304. Comparison of the Properties of the three halogens, chlorine, bromine, and iodine, leads to some interesting results:

Name of Element	Atomic Weight	State	Solubility in One Part of Water at 15°C.	Heat of Formation of Hydrogen Comp.	Heat of Formation of Potassium Comp.
Chlorine .	35.5	Gas	2.4 pt.	22,000 cal.	105,700 cal.
Bromine .	80	Liquid	0.032 pt.	8,446 cal.	95,100 cal.
Iodine . .	127	Solid	0.00015 pt.	−6,400 cal.	80,130 cal.

Chlorine, bromine, and iodine form a natural group of elements. The difference between the atomic weight of bromine and that of chlorine is nearly the same as the

difference between the atomic weights of iodine and bromine. An examination of the table will show that the properties of these elements vary in degree with the atomic weights. Chlorine, bromine, and iodine are very closely analogous to each other in their chemical behavior. The chemical activity of bromine is less than that of chlorine and greater than that of iodine.

305. Heat of Formation. — When a chemical change occurs without the addition of energy, the substances resulting from the reaction usually contain less energy than the original constituents. Chemical energy has been transformed into some other kind of energy. It is most often liberated in the form of heat.

When elements unite to form chemical compounds, the heat evolved or absorbed is called the *heat of formation* of the compound in question. In measuring the heat of formation of any compound, gram-molecular weights (§ 115) are considered, and the quantity of heat is commonly expressed in calories (§ 45). *The heat of formation is the number of calories of heat absorbed or liberated during the formation of a gram-molecular weight of a compound from its elements.*

Hydrogen unites with chlorine to form hydrogen chloride. The simplest equation representing the reaction is:

$$H + Cl \longrightarrow HCl$$

This shows that 1 gram of hydrogen unites with 35.5 grams of chlorine to form 36.5 grams of hydrogen chloride. During the combination, 22,000 calories of heat are evolved. The thermal equation for the formation of hydrogen chloride is then:

$$H + Cl \longrightarrow HCl + 22{,}000 \text{ calories}$$

The heat of formation of hydrogen chloride is 22,000 calories.

When hydrogen combines with iodine to form hydrogen iodide, an absorption of heat occurs. Absorption of heat is indicated by a minus sign. The thermal equation reads:

$$H + I \longrightarrow HI - 6400 \text{ calories}$$

This shows that when 1 gram of hydrogen unites with 127 grams of iodine, 6400 calories of heat are absorbed. The heat of formation of hydrogen iodide is − 6400 calories.

306. Relative Replacement and Heats of Formation. — Let us use the double arrow in the following equation to indicate the two possible directions in which the reaction *might* proceed:

$$HCl + Br \rightleftarrows HBr + Cl$$

Would bromine actually replace chlorine or would the reverse be true? The following generalization has been developed from the study of the heat effects of many chemical changes.

When a chemical reaction takes place without the addition of heat from an external source, that substance which has the greatest heat of formation will tend to form.

The heat of formation of hydrogen bromide is 8446 calories; that of hydrogen chloride is 22,000 calories. Thus more heat is liberated when hydrogen unites with chlorine than is liberated when hydrogen combines with bromine. Therefore, in accordance with the above principle, there is a tendency to form hydrogen chloride, and we should expect chlorine to liberate bromine from hydrogen bromide. Experiment confirms this conclusion. Either chlorine or bromine liberates iodine from hydrogen iodide, because

hydrogen iodide has a lower heat of formation than either hydrogen chloride or hydrogen bromide. By the study of the heats of formation of chemical compounds, we can predict the direction of chemical reactions.

It should be remembered that heat is not the only form of energy into which chemical energy is converted. In voltaic cells, for example, part of the chemical energy is converted into electrical energy. In making thermal measurements, it is necessary to take account of the fact that heat is liberated or absorbed in the physical changes that accompany the act of solution.

Fluorine

307. Activity. — Fluorine belongs to the halogen group, but does not so closely resemble the other members of the group as they resemble each other. A consideration of fluorine has therefore been made to follow a study of the other members of the group.

Fluorine is an element of unusual chemical activity; few substances are not attacked by it. It cannot be isolated in the presence of water, as it unites with the hydrogen in the solution and liberates the oxygen. Furthermore, it cannot be prepared in glass vessels, as it reacts with the glass. The heats of formation of the fluorides are too great to permit of their being easily decomposed by heat. From the statements just made it will be seen that fluorine cannot be prepared by the methods generally employed in the preparation of the other halogens.

308. Preparation. — The problem of isolating pure fluorine puzzled chemists until 1886, when Moissan discovered that a solution of potassium fluoride in anhydrous hydrogen

fluoride conducts the electric current. The apparatus used by Moissan to carry on the electrolysis consisted of a U-tube made of an alloy of platinum and iridium, carrying electrodes composed of the same material, which were insulated from the U-tube by calcium fluoride stoppers (Fig. 115). Moissan subsequently found that a U-tube made of copper could be substituted for the one composed of the expensive alloy mentioned.

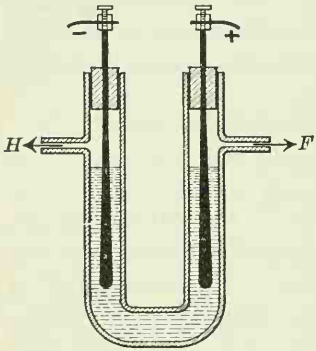


FIGURE 115.

It was very difficult to obtain fluorine in the free state. Finally Moissan accomplished its separation by the aid of this apparatus.

The solution of potassium fluoride in hydrofluoric acid was placed in the U-tube and kept at a temperature near −23° C. during the electrolysis.

Fluorine is liberated at the anode, and passes off through the side arm of the tube surrounding it. Hydrogen is liberated at the cathode. Potassium passes to the cathode, but, on giving up its electric charge, instantly unites with fluorine, forming potassium fluoride, which dissolves in the excess of hydrofluoric acid. The result of this electrolysis is that only the hydrofluoric acid is permanently decomposed.

309. **Properties.** — At ordinary temperatures, fluorine is a nearly colorless gas, much more poisonous than chlorine. Liquid fluorine combines energetically with hydrogen, sulphur, phosphorus, arsenic, some other elements, and many compounds, showing that violent chemical action can take place at a very low temperature.

Under ordinary conditions, fluorine has a greater tendency to form compounds than any other element. Copper when placed in fluorine becomes coated with an insoluble coating of copper fluoride. The fluorides of calcium, strontium, and barium are insoluble. Silver fluoride is soluble. Gold and platinum, which readily form compounds with nascent chlorine, are very slowly attacked by fluorine. No oxide of fluorine is known. It is interesting to compare the properties of fluorine just mentioned with those of chlorine, bromine, and iodine.

Two compounds of fluorine that occur in nature are of importance: calcium fluoride or fluor spar, CaF_2, and cryolite, $3\ NaF \cdot AlF_3$. Cryolite is used as the solvent in the preparation of aluminum by the electrolytic process.

310. Hydrofluoric Acid. — Hydrofluoric acid is prepared by the action of sulphuric acid with fluor spar:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF\uparrow$$

The reaction is commonly carried on in a lead dish.

Pure hydrogen fluoride is a colorless liquid that fumes strongly in air. It dissolves readily in water and aqueous solutions of it are sold in wax bottles. Great care should be exercised in using this acid, as painful sores, difficult to heal, are produced when it comes in contact with the skin. There have been cases where the inhalation of hydrogen fluoride vapor has caused death.

The *chief use* of hydrofluoric acid is in the etching of glass. Glass is composed of silicates, and hydrofluoric acid converts the silica (silicon dioxide) of the glass into a gas, silicon fluoride, and water:

$$SiO_2 + 4\ HF \longrightarrow SiF_4\uparrow + 2\ H_2O$$

Glass is prepared for etching by covering it with a coating of some substance that is not attacked by hydrofluoric acid, such as paraffin or a mixture of beeswax and rosin, and then removing the coating with a sharp instrument from the part to be etched. The etching is accomplished by subjecting the prepared piece to hydrofluoric acid vapor, or by applying to it a water solution of the acid (Fig. 116). When the gas is used the surface of the etching is left dull, while with a water solution it is left glossy. Hydrofluoric acid is used in the finishing of cheap cut glass ware. Sodium and ammonium fluoride solutions also are used for etching glass.

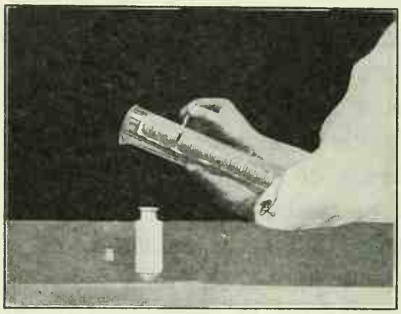


FIGURE 116.

Hydrofluoric acid reacts with glass. The liquid is being painted on places where a wax coating has been scratched away. Thus marks are made on the glass.

SUMMARY

Bromine, atomic weight, 80, resembles chlorine very closely. The chief points of difference are (1) it is a dark-colored liquid and (2) it is less active. In general, bromine reactions resemble those of chlorine, but are of less intensity.

Bromides are found in nature associated with chlorides. Bromine is **prepared** from bromides by a process analogous to that used in the preparation of chlorine from sodium chloride. A mixture of a bromide and manganese dioxide is treated with concentrated sulphuric acid. The manganese dioxide acts as an oxidizing agent on the hydrobromic acid that is formed by the action of the sulphuric acid with the bromide.

Hydrobromic acid is the water solution of hydrogen bromide, which is formed by the action of moderately concentrated sulphuric acid with potassium bromide. There is a marked difference here from the action that occurs in the preparation of hydrochloric acid. This difference is due to the fact that the hydrobromic acid is less stable (*i. e.* has a less heat of formation) than hydrochloric acid. The secondary products formed in the case of hydrobromic acid are mainly sulphur dioxide and free bromine, resulting from the oxidizing action of the sulphuric acid.

Bromine and its compounds are not of great commercial importance. **Bromides are used** in medicine, and free bromine is used in the preparation of certain dyes

Since bromides have smaller heats of formation than the corresponding chlorides, free **chlorine will displace bromine** from bromides. The presence of free bromine in solution may be detected by the color it imparts to carbon disulphide or chloroform.

Iodine, atomic weight, 127, is found as iodides in small quantities in the ashes of sea plants, and associated with sodium and potassium compounds. It is a dark gray solid with the suggestion of a metallic appearance. In its chemical properties, it resembles chlorine and bromine, but it is less active than either. Thus we find that with these three elements, **as the atomic weight increases the activity diminishes**, and the elements lose something of their non-metallic character.

Iodine may be prepared by a process analogous to that used in the preparation of chlorine or bromine.

Hydriodic acid results from the action of moderately concentrated sulphuric acid with potassium iodide, but only a small part of the expected quantity is obtained. The heat of formation of hydriodic acid is so low that this acid is very readily oxidized by the sulphuric acid. Sulphur dioxide, free sulphur, hydrogen sulphide, water, and free iodine may all be formed during this secondary action.

Iodides have a less heat of formation than bromides. Consequently free **bromine will displace iodine** from iodides. Chlorine will do the same thing even more readily.

Fluorine, atomic weight, 19, is the most intensely active element known. Hydrofluoric acid is a stable compound used in etching glass.

The four **halogens, considered as a group**, may be regarded as a nearly perfect example of a chemical family. The properties change in a very definite and regular way with the change in atomic weight.

EXERCISES

1. How does difference in solubility aid in separating bromides from the chlorides of salt deposits?

2. Why should bromine water be kept in a dark place?

3. Write the equations representing the reactions of bromine with zinc, antimony, and hydrogen. Name the products in each case.

4. Account for the odor of sulphur dioxide sometimes obtained when concentrated sulphuric acid is added to a bromide.

5. Prepare a table of the halogens according to the following form:

a	*b*	*c*	*d*	*e*
Elements in order of atomic weights	Atomic weight	Compounds found in nature (Formulas)	Equations for the preparation of element	Physical properties

f	*g*	*h*	*i*
Chemical properties	Relative replacing power in binary compounds	Equations for the preparation of the hydrogen compound	Stability of the hydrogen compound

6. A solution of sodium bromide is treated with an excess of silver nitrate, and 0.65 gram of silver bromide is precipitated. What weight of sodium bromide was contained in the original solution?

7. Define leaching; sublimation; tincture; heat of formation.

8. How would you recover some iodine that had become mixed with sand?

9. Write the three equations that show the relative replacement of bromine, chlorine, and iodine.

10. Why is not sulphuric acid used for the preparation of hydriodic acid?

11. An unlabeled bottle is known to contain either potassium bromide or potassium chloride. How could you tell which was present?

12. What weight of iodine could be obtained from 150 grams of potassium iodide? How much sulphuric acid would be needed for the action?

13. Solutions of hydriodic acid become dark colored on standing. To what substance is the dark color probably due? Explain the action that produces it.

14. What laboratory method is equally good for the preparation of chlorine, bromine, and iodine? Write the equations.

15. Employing the starch test, how would you prove the presence of an iodide?

16. State how opaque graduations could be marked on a blank gas measuring tube.

CHAPTER XXIII

CARBON

311. Unusual Character. — Carbon, though a non-metal, differs in several important respects from the other elements of its class. With hydrogen it forms almost numberless compounds called *hydrocarbons*. Besides these, there are many compounds that are composed of carbon, hydrogen, and oxygen; others are known that contain chlorine, bromine, iodine, nitrogen, sulphur, or some other element. There are so many carbon compounds that the branch of chemistry which deals with them has a special name, *organic chemistry*. Some of the more important organic compounds are treated in Chapter XXXVIII.

312. Importance of Carbon in Nature. — Every living thing, plant or animal, contains carbon in its tissues in the form of organic compounds. The higher plants always contain a large amount of cellulose, a compound of carbon, hydrogen, and oxygen. Cotton fiber is the purest form of cellulose known.

The muscular tissue of animals is composed of a class of bodies known as *proteins*. They contain carbon, hydrogen, oxygen, and nitrogen, with a very small quantity of other elements. The *fat* of animals is composed of carbon, hydrogen, and oxygen.

313. Occurrence. — In the uncombined form, carbon is found as coal, graphite, and diamond. In addition to its occurrence in organic compounds, the element is also found in *carbon dioxide* of the atmosphere, and very abundantly in the *carbonates* of certain metals, especially calcium and magnesium. Marble and limestone are two different varieties of calcium carbonate. A considerable part of the earth's crust is made up of these materials.

314. Coal. — There are two chief forms of coal and several less important varieties. None of them is pure carbon. The most important factor in determining the fuel value of coal is the amount of noncombustible matter, commonly called ash. This varies widely in different grades. Anthracite or hard coal contains over 80% of uncombined carbon. It usually contains a small amount of moisture. Anthracite coal is generally graded in size by screening. The smaller sizes contain more ash than large sizes. Bituminous or soft coal (Fig. 117 *c*) contains more hydrogen and ash than anthracite coal. The hydrocarbons can be driven off as gases by heating the coal without access of air. This operation furnishes a means of making one kind of illuminating gas.

Coal is fossil vegetable matter. During a part of the earth's history, known in geology as the carboniferous period, vegetation flourished to a remarkable extent. Much of this vegetable matter was buried under beds of mud and sand. In this condition, it underwent very slow partial decomposition. A large part of the hydrogen and oxygen was given off, and the remainder, which was left as coal, consists mainly of carbon. In anthracite coal the decomposition has proceeded further than in bituminous coal.

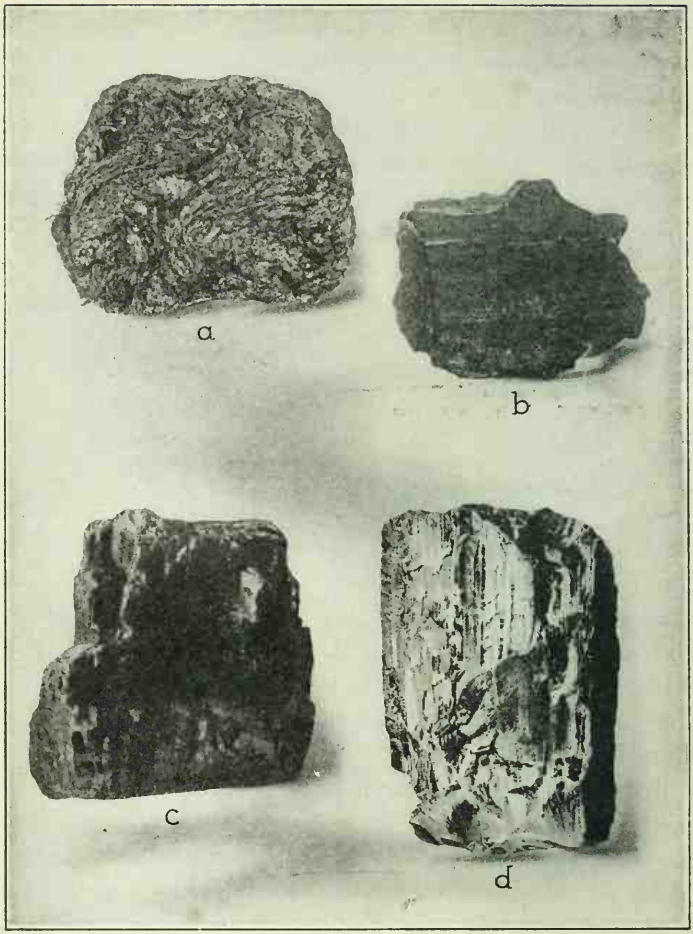


FIGURE 117.

Fuels that have been formed from deposits of vegetable matter. *a*, peat; *b*, lignite; *c*, soft coal; *d*, hard coal.

The dividing line between bituminous and anthracite coal is not a sharp one; varieties are found that are known as semi-bituminous.

Some forms of coal contain even less uncombined carbon than does the bituminous variety. Cannel coal and lignite belong to this class. Lignite exhibits much of the structure of the wood from which it was derived (Fig. 117, *b*). Peat is moss or other loose vegetable matter that, to a slight extent, has undergone a change like that by which coal was formed (Fig. 117, *a*). When cut from the bogs, peat contains a large amount of water, which must be removed

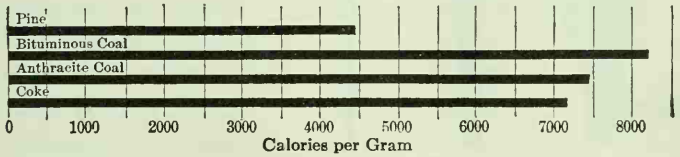


FIGURE 118.

Weight for weight, bituminous (soft) coal gives the most heat of these common fuels.

before it can be used as a fuel. Figure 118 shows the relative heating value of coal, wood, and coke.

315. Lampblack. — Lampblack, a form of soot, is practically pure carbon. It is best made by burning hydrocarbon oils with a limited supply of air. The operation is analogous to that which takes place when a kerosene lamp smokes. The hydrogen of the oil burns, but much of the carbon remains unburned because of the lack of oxygen. The unburned carbon is deposited as a soft, amorphous, slightly greasy powder. Lampblack is used as a pigment in making paint and some inks, including printers' ink.

Large quantities of lampblack, called *carbon black*, are made from natural gas by using machines of special design.

One of these lampblack machines (Salsburgh patent) is shown in the broken drawing, Figure 119. The cast-iron disk (*D*), about four feet in diameter, is mounted on a hollow shaft. The burner (*G*) is mounted close to the disk in such a position that the flames from the tip will be divided, half of the flame depositing a thin coating of soot, or lampblack, on the concave surface, and the other half of the flame depositing a thin coating on the convex surface of the disk.

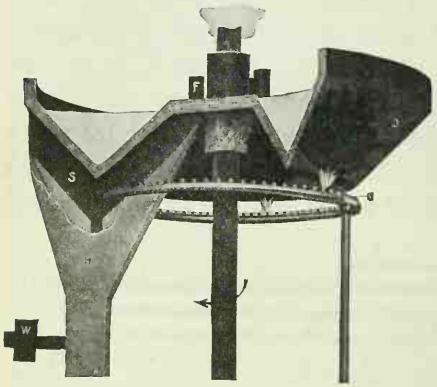


FIGURE 119.

Any one who has seen a smoked lamp chimney might have invented this machine. Gas flames "smoke" (deposit soot on) a water-cooled, revolving iron trough. It is shown "broken away," in order that you may see how the water does the cooling.

As the disk revolves slowly in the direction of the arrow, the scraper (*S*) removes the lampblack from the disk and the black powder falls through the hopper (*H*). The lampblack is sifted and prepared for sacking. The top of the disk is kept full of running water, which cools the disk, and then empties into the hollow shaft.

316. Wood Charcoal. — Wood charcoal is made by heating wood without access of air. To a certain extent, this operation resembles the natural process by which coal was formed. The hydrogen, oxygen, nitrogen, and some of the carbon which the wood contains pass off in the form

of various simpler compounds. The operation is known as *destructive distillation* (Fig. 219, § 543). The charcoal that remains is uncrystallized in form, and retains the cell structure of the wood from which it was formed. Charcoal is not pure carbon, as is shown by the fact that it leaves an ash on burning.

317. Boneblack, or animal charcoal, is obtained by heating bones without access of air. Bones contain both mineral and animal matter. The animal matter, consisting of carbon compounds, is converted into charcoal by destructive distillation; the mineral matter is chiefly calcium phosphate. Boneblack is extensively used for filtering purposes. It has the power of taking up both coloring matter and gases from solution. This is characteristic of nearly all amorphous substances. Other forms of amorphous carbon have the same property in a less degree.

The most important use of boneblack is in the decolorization of sugar and oils. When sugar solutions in the refinery are decolorized by filtering through boneblack, the coloring matters adhere to the surface of the boneblack. *Adsorption* is the name given to such an action. Boneblack is so porous that it presents an enormous amount of surface for the adsorption of the coloring matters.

318. Coke. — Coke is obtained by the destructive distillation of bituminous coal. It is also obtained in the manufacture of one kind of illuminating gas known as *coal gas*. In the United States, nearly 50 million tons of coke are produced yearly and used as a fuel and as a reducing agent in the working of metals. The collection of the by-products is an important feature of the operation of the modern coke oven.

Oil coke collects in the retorts used in distilling petroleum. Oil coke is a good and durable conductor of electricity and is used for making carbon rods for arc lights and dry cells.

Allotropic Forms

Among all the varieties of carbon three distinct allotropic forms are recognized. These are amorphous carbon, graphite, and diamond.

The three allotropic forms can each be burned in oxygen, if raised to a sufficiently high temperature, with the formation of nothing but carbon dioxide. This fact proves that the three substances are the same element in different forms. They differ widely in physical properties and in the ease with which they burn.

319. Amorphous Carbon. — The name, *amorphous carbon*, means that it is without crystalline structure. Its density is low; it is generally soft, and it does not conduct an electric current very well. These properties cannot be specified definitely because they vary according to the temperature to which the element has been subjected. Amorphous carbon burns with comparative ease. The different varieties of charcoal, coal, and coke are impure forms of amorphous carbon. Lampblack is the purest form ordinarily obtained. Its uses have already been mentioned (§ 315).

320. Graphite. — Graphite is a crystalline form of carbon. There are a number of natural deposits of graphite, the best coming from Ceylon, Siberia, and New York. Graphite is now produced artificially by heating anthra-

Edward Goodrich Acheson is the inventor of many important processes associated with the graphite and carbon compounds. He is famous chiefly as the discoverer of carborundum, artificial graphite, and deflocculated graphite. In connection with these industries, he has had a great deal to do with the development of electric furnaces. He has invented graphitized anodes, which are much more durable than carbon electrodes in electrolytic furnaces. To meet the need for a highly refractory material he invented siloxicon, a compound of carbon, silicon, and oxygen, which resists fusion even at very high temperatures. He was awarded the Perkin Medal of the Society of Chemical Industry in January, 1910.

cite coal in an electric furnace. The crystals of graphite appear as minute scales or plates, which present a very good sliding surface. To this property is due the use of graphite as a lubricant. Artificial graphite may also be prepared in the form of extremely finely divided powders, that will remain suspended in water or in oil (deflocculated graphite). Graphite differs from other forms of carbon in being very soft, in conducting the electric current readily, and in having a very high kindling temperature. Like all forms of carbon, it is practically infusible. This refractory nature of graphite permits its use in crucibles for melting metals. Its resistance to heat and its electrical conducting power cause it to be extensively used for the melting pots and electrodes of electric furnaces. Graphite is also used for making lead pencils. The varying degrees of hardness in the pencil are secured by mixing the graphite with clay. Another use of graphite is to prevent the formation of scale in steam boilers.

321. Diamond. — Diamond, the third form of carbon, is also a crystallized variety. It is found as octahedral crystals, sometimes colorless and transparent, sometimes tinted or even black. The diamond differs from the other allotropic forms in being extremely hard. It is the hardest substance known. Like graphite, it burns with difficulty. The beauty of diamonds is due to the fact that light in passing through them is highly refracted so that a sparkling play of color results. This effect is heightened by cutting the surface of the stone into numerous facets. The value of a diamond depends largely on its color and its brilliancy. Discolored stones are employed in instruments used for cutting hard materials.

Microscopic diamonds have been made artificially, but such artificial diamonds have never been obtained clear or of appreciable size.

322. Chemical Properties. — The *physical properties* of carbon have been described in discussing the allotropic forms of the element.

None of the forms of carbon reacts with either acids or bases. They are all insoluble in ordinary solvents. Melted iron dissolves carbon to a certain extent.

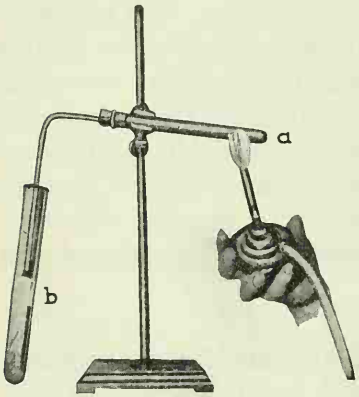


FIGURE 120.

Carbon combines with the oxygen of the copper oxide in (*a*). The carbon dioxide thus formed turns limewater milky (*b*).

Carbon has a great tendency to unite with oxygen at moderately high temperatures. It not only burns in oxygen, but it also unites with the oxygen that is held in combination with other elements. On this account, carbon makes an excellent reducing agent. The reaction of carbon with copper oxide illustrates this property. When the mixture is heated in a hard glass test tube (Fig. 120, *a*) and the gas is led into limewater (Fig. 120, *b*), a white precipitate of calcium carbonate indicates the presence of carbon dioxide, and metallic copper is produced:

$$2\,CuO + C \longrightarrow 2\,Cu + CO_2\uparrow$$

Enormous quantities of coke are used in the reduction of metals, particularly iron and copper, from their ores.

323. Reactions at High Temperatures. — In spite of the fact that carbon forms so many different compounds with hydrogen, it unites directly with this element only at a high temperature, and then very slowly. By using the high temperature of an electric furnace, carbon can be made to unite with many metals and some non-metals.

The electric arc furnace is a device for producing very high temperatures by using a large arc between carbon terminals. The arc consists of carbon vapor, which

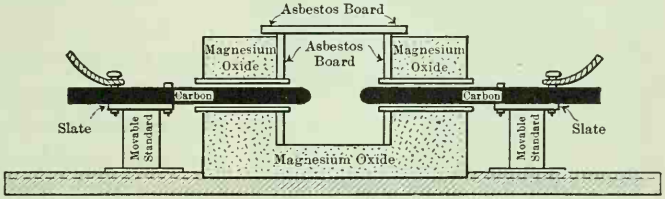


FIGURE 121.

The current is turned on while the carbon rods touch each other. When they are pulled apart, an arc of intensely hot carbon gas forms between them.

conducts the current over the gap between the carbons, and the resistance is so great that much heat is developed. A temperature of about 3000° C. may be obtained, and the reactions that occur in the electric furnace are due to the high temperature. The electric current does not directly play any part in the reactions. A simple laboratory form of arc furnace is shown in Figure 121.

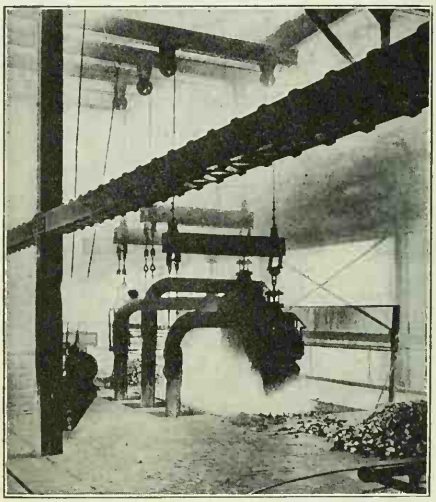
The intense heat of an electric furnace makes carbon react with lime (calcium oxide), to form calcium carbide:

$$CaO + 3\,C \longrightarrow CaC_2 + CO\uparrow$$

Calcium carbide is used to prepare *acetylene*, a gas that makes an excellent illuminant and heat producer (§ 342).

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

Carborundum (§ 369), silicon carbide, a very useful abrasive, is made by heating sand (silicon dioxide) and carbon in an electric resistance furnace (Fig. 155):



Courtesy of American Cyanamid Co.

FIGURE 122.

A huge modern electric furnace for the making of calcium carbide.

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO\uparrow$$

When carbon is similarly heated in sulphur vapor, the two elements combine to form carbon disulphide:

$$C + 2\,S \longrightarrow CS_2$$

Carbon disulphide is a heavy, inflammable liquid, with a disagreeable odor, if not pure. It is a valuable solvent for rubber, and is extensively used in the manufacture of artificial silk and to destroy vermin.

324. Uses of Carbon. — The uses of carbon have been pointed out in the discussion of the properties of the various forms of the element. Coal is the principal source of artificial heat. Anthracite is, in general, the most desirable

kind of coal, because it burns with practically no flame and without the formation of soot. It burns more slowly and gives a more uniform heat than does bituminous coal. The consumption of anthracite coal is relatively small; about 75,000,000 tons are used annually, and its use is confined to a few localities.

There is over seven times as much bituminous coal produced as anthracite; it is much cheaper, and, weight for weight, produces more heat. Coke burns like anthracite coal and is sometimes used in its place. In warm countries charcoal is often the only fuel used. Many metals are separated from their ores by the aid of coke as the reducing agent. Iron is obtained in this way. The making of coke from bituminous coal for this purpose is an important industry. Charcoal and boneblack are both used to remove gases and coloring matter from solutions. Impure water is sometimes passed through charcoal filters for purification. This method, while it may suffice for the removal of impurities which can be seen or smelled, is not to be relied upon for the removal of disease germs.

SUMMARY

Carbon is a non-metallic element characterized by the **enormous number of compounds** it forms with the non-metallic elements, especially hydrogen, oxygen, and nitrogen.

Carbon is an **inert element at ordinary temperatures**; at higher temperatures it combines readily with oxygen and with a few other elements; at the temperature of the electric furnace it reacts with lime, forming calcium carbide and with silicon dioxide to form carborundum.

Amorphous carbon, graphite, and diamond are the three **allotropic forms of carbon.** These allotropic forms differ widely in

physical properties, but all yield the same product when burned in sufficient oxygen.

Carbon is found combined in the tissues of every living thing, in the carbon dioxide of the atmosphere, and in metallic carbonates. Uncombined, it occurs as coal, graphite, and diamond.

Aside from ash, anthracite **coal** is nearly all carbon, and bituminous coal is about two thirds carbon and one third hydrocarbons. Cannel coal and lignite are relatively poor in carbon.

The **uses of** the commercial forms of **carbon** are:

Coal: fuel and manufacture of illuminating gas;
Lampblack: paint and printers' ink;
Wood charcoal: fuel and filtering;
Boneblack: filtering and decolorizing sugar and oils;
Coke: fuel, ore reducer, and manufacture of water gas;
Graphite: lead pencils, lubricant, crucibles, and electrodes for high temperatures;
Diamond: gem and abrasive.

EXERCISES

1. Tell how the carbon in your muscular tissue is indirectly derived from the air.

2. How does anthracite coal differ from bituminous coal in appearance and in chemical composition?

3. Why does soft coal make such a smoky fire?

4. Why is anthracite coal preferred for household use?

5. Prepare a comparison of fuels, using a tabular form containing the headings: Kind of Fuel; Approximate Composition; Advantages; Disadvantages.

6. Explain why fence posts are sometimes charred at the end before being placed in the ground.

7. What properties of lampblack make it suitable for printers' ink and for paint?

8. What happens when a solution of brown sugar is filtered through boneblack?

9. What kind of carbon is used in batteries?

10. State briefly how you could distinguish between pulverized charcoal and manganese dioxide.

11. What three conditions are necessary for ordinary burning?

12. Why does water put out a fire?

13. Why is a candle extinguished by blowing?

14. In working with compressed air it is found that combustible materials burn more readily than usual. Explain.

15. What chemical reaction proves that the three allotropic forms of carbon are varieties of the same element?

16. Why is graphite used in: (*a*) lead pencils; (*b*) lubricants; (*c*) crucibles for melting metals; (*d*) electrodes for electric furnaces?

17. How many liters of oxygen are required for the complete combustion of 10 liters of acetylene gas? How many liters of air are required?

18. Write three chemical equations that illustrate the action of carbon at high temperatures.

CHAPTER XXIV

OXIDES OF CARBON

Carbon Dioxide

325. Occurrence. — There are three very important sources of carbon dioxide: the decay of vegetable and animal matter; the oxidation constantly going on in animals, and to a much smaller extent in plants; the combustion of all ordinary fuels, such as wood, coal, and gas. These fuels consist largely of carbon; this, on burning, combines with oxygen, forming carbon dioxide:

$$C + O_2 \longrightarrow CO_2$$

Hence carbon dioxide is always present in the air, usually to the amount of four parts in ten thousand (§ 236). This percentage would be much higher were it not for the fact that plants are constantly taking in carbon dioxide, building the carbon into their tissues, and returning the oxygen to the air.

Natural waters also very commonly contain carbon dioxide; in some spring waters the gas is dissolved in such quantities that they are effervescent, that is, they give off gas in bubbles unless kept in tightly closed vessels. Carbon dioxide is also given off by volcanoes and from other subterranean sources, and from fermenting liquids. It is sometimes found in coal mines, where it is known as *choke damp*.

326. Preparation. — Carbon dioxide is most conveniently prepared in a pure state by the action of a carbonate with an acid (Fig. 123). Calcium carbonate, which occurs abundantly in the forms of *limestone*, *marble*, and *chalk*, is used on account of its cheapness; and, on a manufacturing scale, sulphuric is the acid selected. But this is not convenient when the carbon dioxide is needed in small quantities, as in the laboratory, because the calcium sulphate, which is formed in the action, is insoluble and remains as a coating on the pieces of carbonate, thus hindering the reaction. Hydrochloric acid gives good results because calcium chloride is very soluble in water. The equation representing the reaction is:

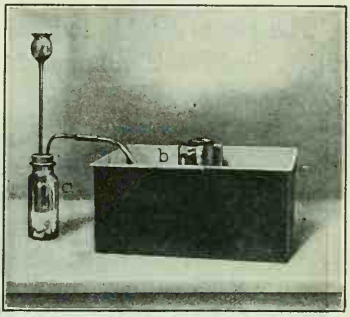


FIGURE 123.

In (*a*) carbon dioxide is generated by the interaction of calcium carbonate and dilute hydrochloric acid. Although the gas is somewhat soluble, there is no great loss when it is collected over water (*b*).

$$CaCO_3 + 2\,HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

To remove any hydrochloric acid that may be carried over, the gas is allowed to bubble through water. The gas is collected by the downward displacement of air, or over water.

327. Physical Properties. — Carbon dioxide is a colorless gas with almost no taste or odor. It is about one and one half times as dense as air, so that it can be poured like water from one vessel to another. Carbon dioxide is some-

times given off from soil and water; and in wells, caves, and mines it frequently collects, because the lack of air movement permits the relatively heavy gas to settle and accumulate.

The gas is soluble in water, which, at ordinary temperatures, dissolves a volume of carbon dioxide equal to its own

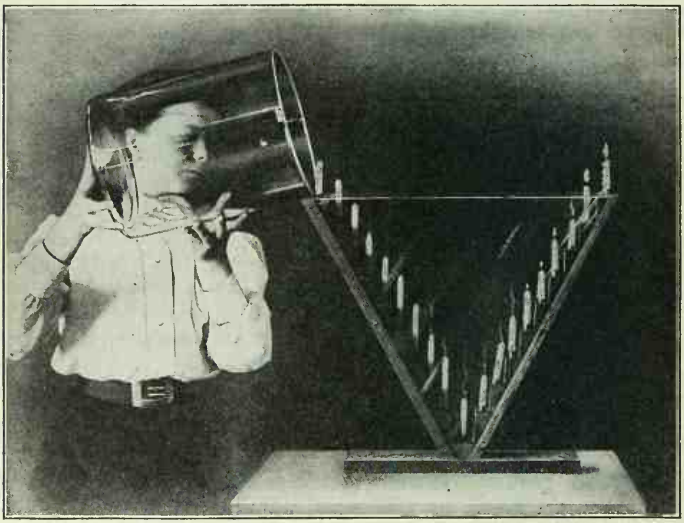


FIGURE 124.

Carbon dioxide is such a heavy gas that it can be poured into a trough as if it were water. The extinguished candles show the path of flow of the heavy gas.

volume. Under increased pressure, water dissolves a greater weight of the gas; if the pressure is removed, the gas is slowly given off, since the weight of a gas which a given volume of a liquid will dissolve is directly proportional to the pressure. An illustration of this property is found in effervescent beverages, which always contain dissolved carbon dioxide.

Carbon dioxide can be liquefied by pressure at ordinary temperatures and the liquid is sold in steel cylinders.

328. Chemical Properties. — Carbon dioxide is chemically inactive toward most substances. It is the product of the complete oxidation of carbon, an action which occurs with the liberation of a great amount of energy. Carbon dioxide can, however, be reduced by very active reducing agents, such as burning potassium, sodium, or magnesium. These elements unite with oxygen and set carbon free.

Carbon dioxide does not support combustion (Fig. 124). This property makes it very valuable for use in extinguishing fires.

329. Carbon Dioxide in Air. — Under certain conditions the amount of carbon dioxide in the air may go much above the normal. This does not interfere with either combustion or the process of breathing, unless the increase in carbon dioxide in the air is accompanied by a corresponding decrease in oxygen, which may or may not be the case. The per cent of carbon dioxide in the air is, therefore, not a measure of its fitness for breathing, except as an index to ventilation.

Because of its relation to life, the most important reaction of carbon dioxide is one that occurs in the leaves of plants. There it reacts with water under the influence of light and chlorophyl, forming starch and setting oxygen free:

$$6\ CO_2 + 5\ H_2O \longrightarrow C_6H_{10}O_5 + 6\ O_2 \uparrow$$

The water in this reaction is taken by the roots of the plant from the soil, and the carbon dioxide is taken from the air by the leaves.

330. Carbonic Acid. — The solution of carbon dioxide has a slightly acid reaction and forms carbonates with bases. Carbonic acid is extremely unstable, and, like ammonium hydroxide, has never been isolated, but the formation of carbonates indicates the presence of H^+ ions and CO_3^{--} ions. We may write the equation:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + H^+ + CO_3^{--}$$

Carbon dioxide passed into a solution of a base produces the corresponding carbonate. As calcium carbonate is insoluble, calcium hydroxide (limewater) is used as a test for the presence of carbon dioxide. When carbon dioxide is first passed into limewater, the mixture becomes milky, and on standing the precipitate of calcium carbonate settles:

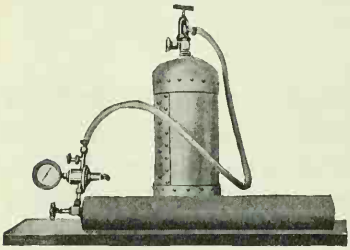


FIGURE 125.

The long cylinder contains liquid carbon dioxide. This passes as a gas into the water contained in the soda fountain tank.

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2\,H_2O$$

If the passage of carbon dioxide is continued, the precipitate dissolves. This is because it has been converted into calcium bicarbonate, which is soluble in water:

$$H_2CO_3 + CaCO_3 \longrightarrow Ca(HCO_3)_2$$

331. Uses of Carbon Dioxide. — As an easily soluble, nonpoisonous gas, carbon dioxide is extensively employed in the manufacture of effervescent beverages. Soda water

is water into which carbon dioxide has been forced under pressure (60 lb. or more). It effervesces when drawn. Seltzer, vichy, and other mineral waters are produced artificially by charging with carbon dioxide solutions whose composition is similar to that of the original spring.

The raising of bread and most other forms of *leavening* generally depend on the expansion of bubbles of carbon dioxide by heat. The carbon dioxide is generated by yeast or by baking powder, which consists of a mixture of sodium bicarbonate (baking soda) and a material of acid reaction; for example, acid potassium tartrate, $HKC_4H_4O_6$ (cream of tartar):

$$NaHCO_3 + HKC_4H_4O_6 \longrightarrow NaKC_4H_4O_6 + H_2O + CO_2\uparrow$$

The compound, sodium potassium tartrate, $NaKC_4H_4O_6$, is known as Rochelle salts.

Liquefied carbon dioxide is used at soda fountains to make soda water. It is also used in place of ammonia in refrigerating processes, particularly on ocean vessels where the escape of ammonia would be dangerous.

One type of *fire extinguishers* (Fig. 126) contains a device for generating carbon diox-

Inside view. Outside view.

FIGURE 126.

Turn this quick-acting fire extinguisher upside down and a large quantity of carbon dioxide gas is quickly produced. Its pressure is sufficient to throw a stream of liquid for a considerable distance.

ide rapidly, as by mixing sulphuric acid with a solution of sodium bicarbonate when the apparatus is inverted. The pressure of the gas forces on the fire a stream of water that contains bubbles of carbon dioxide. In chemical engines the pressure of carbon dioxide is often used to throw a stream of water.

Courtesy of the Foamite Firefoam Co.

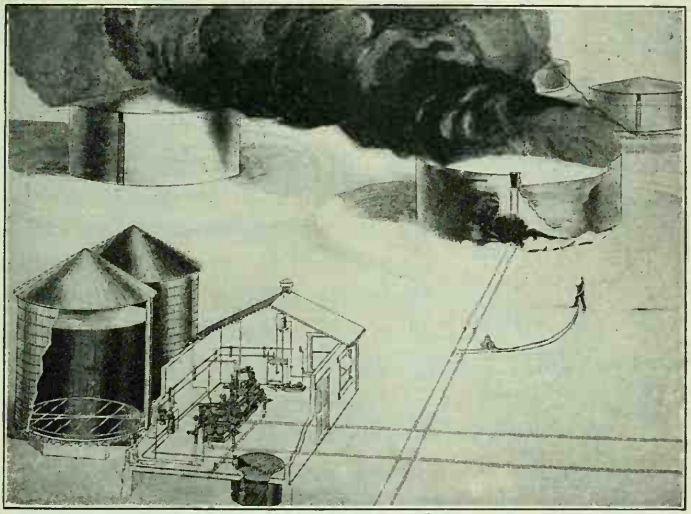
FIGURE 127.

This man is plastering the barn with a foam that contains carbon dioxide. This would prevent the building from burning in much the same way that a woolen blanket or rug puts out a small fire — by excluding oxygen.

332. Foamite. — There has recently been perfected an extremely ingenious and efficient method for extinguishing oil fires and other fires that have not gained great headway. The fundamental basis of the foam system of fire extinguishing is the use of solutions that, when mingled together, will create a large volume of carbon dioxide gas confined in tough, durable bubbles of foam, easily applied and readily adhering to any burning surface. The carbon dioxide is generated by the reaction between solutions of aluminum sulphate and sodium bicarbonate.

$$Al_2(SO_4)_3 + 6\,NaHCO_3 \longrightarrow 3\,Na_2SO_4 + 2\,Al(OH)_3\downarrow + 6\,CO_2\uparrow$$

Foamite is a substance obtained by the second extraction of licorice root. It is mixed with the sodium bicarbonate solution. Foamite plays no part in the chemical reaction, but the aluminum hydroxide and the foamite on coming together form a viscous fluid having a very low surface tension, which the carbon dioxide blows into a foam that is tough and du-



Courtesy of the Foamite Firefoam Co.

FIGURE 128.

Showing how two pipes convey the solutions used in putting out an oil-tank fire by the Foamite method.

rable. The solutions are mixed as they are played on the burning surface, where the mixture spreads out in a thick blanket of tough carbon dioxide foam, resembling thick whipped cream in appearance and consistency. Heat converts the aluminum hydroxide on the surface of the foam into aluminum oxide. There is practically no transference of heat through the foam. The foam does not soak

in and cause damage as water does, nor does it injure the material to which it is applied. No claim is made that this method will enter into competition with a city fire department in the case of ordinary conflagrations. Nothing thus far developed will equal foamite for putting out an oil fire, and it has decided advantages for use in cases of fire in buildings before the fire has gained much headway.

Carbon Monoxide

333. Preparation. — Carbon monoxide differs from carbon dioxide in containing one atom of oxygen instead of two. It can be prepared by the reduction of carbon dioxide. This can be accomplished by passing a current of carbon dioxide over carbon heated to redness. The carbon acts as a reducing agent:

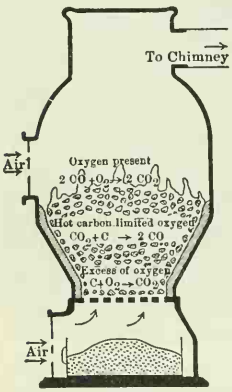


FIGURE 129.

Showing how there may be three distinct chemical actions going on in a coal stove.

$$CO_2 + C \longrightarrow 2\,CO$$

This action takes place in a coal fire. The carbon dioxide, formed near the bottom, is reduced by the hot coal above to carbon monoxide, which is often seen burning at the top of the fire (Fig. 129).

In the laboratory, carbon monoxide is best made by the decomposition of formic acid (Fig. 130). Warm sulphuric acid is slowly dropped into formic acid. The sulphuric acid, by its dehydrating power, induces an action as follows:

$$H(CHO_2) \longrightarrow CO\uparrow + H_2O$$

The water is absorbed by the sulphuric acid. By a similar decomposition, oxalic acid gives carbon dioxide when treated with sulphuric acid:

$$H_2C_2O_4 \longrightarrow CO\uparrow + CO_2\uparrow + H_2O$$

In this case it is necessary to remove the carbon dioxide from the mixed gases. This may be accomplished by passing them through a concentrated solution of potassium hydroxide.

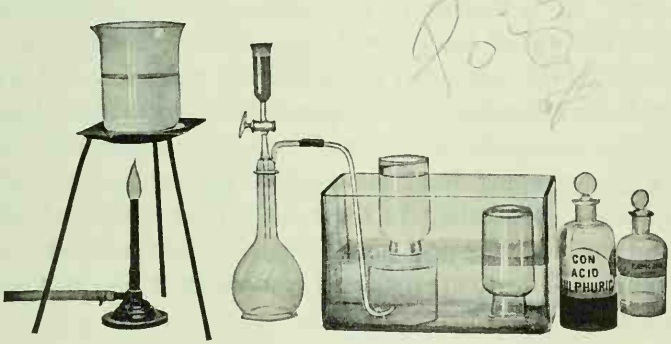


FIGURE 130.

Warmed concentrated sulphuric acid by its dehydrating power decomposes formic acid. Carbon monoxide is liberated.

334. Physical Properties. — Carbon monoxide is a colorless, odorless gas. It is slightly lighter than air and is nearly insoluble in water. It is extremely poisonous; a very small percentage in the air causes headache, and a larger amount may cause death.

335. Chemical Properties. — Under ordinary conditions the monoxide burns in air with a blue flame:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

If both the carbon monoxide and the air are absolutely dry, however, combustion does not take place. Carbon monoxide acts as a powerful reducing agent. The reduction of iron oxide in a blast furnace is largely due to it.

336. Physiological Properties. — Carbon monoxide prevents the oxygen of the air from uniting with the hæmoglobin of the red blood corpuscles, by entering itself into combination with the hæmoglobin to form a stable compound. It is because of this action that a comparatively small amount of the gas will cause death. The compound formed in the corpuscles has a brilliant red color, and is so stable that it can be detected in a body years after death. Carbon monoxide is the chief poison in illuminating gas, the gas escaping from stoves, and the exhaust of automobiles. Fortunately in these cases it is associated with compounds having pronounced odors. In spite of this fact, sickness and death are frequently caused by carbon monoxide poisoning.

SUMMARY

Carbon dioxide is formed in the vital processes of plants and animals, and in ordinary combustion.

It is prepared commercially by the reaction of acids with carbonates.

Carbon dioxide is colorless, slightly soluble in water, and suffocating but not poisonous.

One liter (standard conditions) weighs 1.98 grams.

It reacts with soluble bases, forming carbonates. Small quantities render limewater turbid; an excess of the dioxide causes the precipitate to dissolve by changing it to a soluble bicarbonate.

Carbon dioxide is used in charging beverages, in fire extinguishers, and in ice machines.

Carbon monoxide is formed by:

(1) the reduction of the dioxide;
(2) the reaction of steam and red-hot coal;
(3) the dehydration of formic acid or oxalic acid.

Carbon monoxide is lighter than air, and is very poisonous. One liter (standard conditions) weighs 1.26 grams.

It burns with a pale blue flame, forming the dioxide.

EXERCISES

1. How can it be shown that there is carbon dioxide in the air?

2. Give three ways in which carbon dioxide is produced in nature. How is it commonly made in the laboratory? Write the equation. Write an equation illustrating the use of the same process but with different materials.

3. Why is hydrochloric acid preferred to sulphuric acid in preparing carbon dioxide from calcium carbonate?

4. Why does soda water effervesce when taken from the tank?

5. Describe three important uses of carbon dioxide, and state the properties on which each use depends.

6. Explain how a chemical fire extinguisher puts out a fire.

7. How could you prove that there is carbon in alcohol?

8. By what process may carbon monoxide be obtained from carbon dioxide? Account for the explosions that frequently occur in coal stoves shortly after coal is added. State how these explosions may be avoided.

9. How could you distinguish carbon dioxide from the monoxide?

10. Write the equation for the reaction you would expect if carbon monoxide were passed over hot copper oxide.

11. How would you determine whether a gas were hydrogen or carbon monoxide?

12. Why is it that such a large percentage of the cases of asphyxiation from water gas result fatally?

13. Explain how cases of asphyxiation occur when working in a closed garage in which an automobile engine is running.

14. How many grams of calcium nitrate can be obtained by adding sufficient nitric acid to 15 grams of pure calcium carbonate?

15. (*a*) What weight of carbon dioxide is required to precipitate completely as calcium carbonate the calcium in 1 gram of calcium hydroxide?

(*b*) What volume will this weight of carbon dioxide occupy at room temperature and 760 mm.? (One liter of CO_2 at room temperature and 760 mm. weighs 1.90 grams.)

(*c*) Assuming that each bubble of carbon dioxide contains 0.3 c.c., how many bubbles will be required; and assuming that they pass at the rate of 5 per second, how long will the operation take?

16. How many grams of sulphuric acid reacting with an excess of sodium carbonate are required to produce 200 grams of carbon dioxide (CO_2)?

17. Calculate how many liters of carbon dioxide, at standard conditions, can be obtained by treating 45 grams of pure marble with acid.

18. It has been calculated that an average man exhales 464.5 liters (standard conditions) of carbon dioxide in a day. Cal-

culate how many grams of starch a plant could make from this.

19. Write the equation for the reaction that takes place in the fire extinguisher shown in Figure 126.

20. In the Foamite method of fire extinguishing, explain the use of: (*a*) the solutions of sodium bicarbonate and aluminum sulphate; (*b*) the foamite.

21. Write the formula for (*a*) baking soda; (*b*) cream of tartar. Write the equation for the reaction that takes place when these two substances are used in a baking powder. What causes the dough to rise?

22. What is the action of the concentrated sulphuric acid on the formic acid in the preparation of carbon monoxide? Write the equation.

23. Carbon monoxide passed over warm calcium hydroxide reacts:

$$CO + Ca(OH)_2 \longrightarrow H_2 + CaCO_3$$

How does the volume of carbon monoxide compare with that of the hydrogen?

CHAPTER XXV

GASEOUS AND LIQUID FUELS

337. Natural Gas. — In many parts of the world fuel gases issue from the ground, or may be obtained from wells bored to the gas-containing rock. Such *natural gas* is largely methane, CH_4, mixed with other hydrocarbons and some nitrogen. In burning, carbon dioxide and water (steam) are formed.

$$CH_4 + 2\,O_2 \longrightarrow CO_2\uparrow + 2\,H_2O\uparrow$$

The convenience, ease of distribution, cleanliness, and efficiency of heating by gaseous fuels has led to the introduction of several methods of producing fuel gases.

338. Destructive Distillation. — When soft coal is heated in the absence of air, volatile substances pass off, and coke is left as a residue. *The process of decomposing complex organic substances by heat in closed vessels and condensing the vapor of the liquid products is termed destructive distillation.* This process is used for the production of coal gas.

339. Coal Gas. — The production of coal gas is carried on in retorts heated by coke or gas (Fig. 131). From the retorts the gas passes into:

(*a*) the *hydraulic main*, a device which prevents the backward flow of the gas when a retort is opened, and which incidentally extracts part of the tar;

(*b*) a *condenser*, where, by cooling, more tar is condensed;

(*c*) a *tar extractor*, which removes the remainder of the tar by causing the gas to impinge on sheets of metal;

(*d*) *scrubbers*, horizontal cylinders, where ammonia and cyanogen compounds are absorbed in liquids, which are kept in motion by paddle-wheels;

(*e*) *purifiers*, containing ferric oxide, to remove hydrogen sulphide. The purified gas is measured by a large gas meter and stored in a *gas holder*.

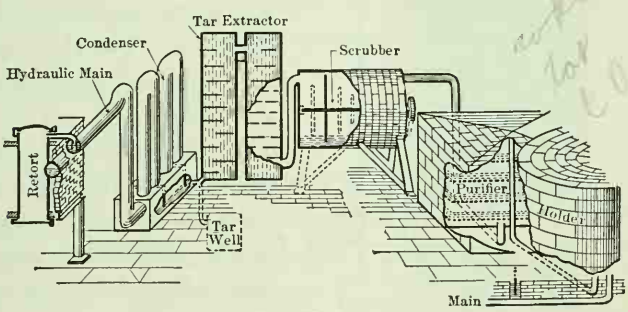


FIGURE 131.

A diagram to show the apparatus used to make illuminating gas from soft coal, and how the valuable by-products are separated.

Coal gas is chiefly a mixture of hydrocarbons. It burns with a luminous flame. A pound of good bituminous coal will yield about five cubic feet of coal gas, so it can hardly be considered a cheap fuel. It has been largely displaced by water gas.

340. Water gas is produced by the reduction of steam by heated carbon:

$$C + H_2O \longrightarrow H_2\uparrow + CO\uparrow$$

As this mixture of carbon monoxide and hydrogen burns with a non-luminous flame, the gas, if it is to be used for lighting, must be enriched by an addition of gaseous hydro-

carbons obtained from petroleum or other sources, such as benzene.

Figure 132 shows a generator in which the two operations are combined. Coal in the lower chamber is burned to incandescence by a blast of air. At first, the hot gases pass up through the side pipe and out at *C*. But after combustion is well under way they are led down through the *carburetor*, and up through the *superheater* and out at *C'*. The brick checkerwork which these two chambers contain is thus heated. When the desired temperature is reached, the first part of the operation, called the *blow*, is terminated. This lasts about five minutes.

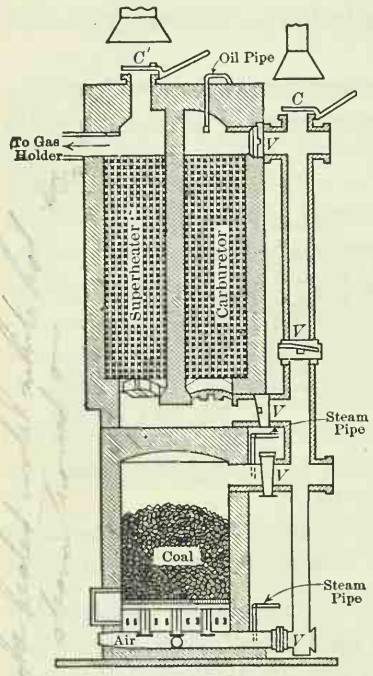


FIGURE 132.

To make water gas, air and steam must be blown alternately through hot coke or hard coal. The upper part of the apparatus serves to make gases from petroleum a permanent part of the mixture. These give the gas illuminating power.

Then steam instead of air is blown through the incandescent coal, and carbon monoxide and hydrogen are formed. Oil is sprayed into the carburetor, and is decomposed by the heat into gases of high illuminating power that mix with the hydrogen and carbon monoxide gas. The decomposition of the oil vapor is con-

tinued and the mixture made uniform in the superheater. The enriched gas passes out of the side pipe at the top of the superheater. This second operation, known as the *run*, also lasts about five minutes and alternates with the blow.

The various valves (V) shown in the diagram control the passage of the gases so that the temperature in any part of the generator can be regulated.

A pound of coal will produce about 25 cubic feet of water gas. This may be enriched so as to be as luminous as coal gas, but for use in Welsbach burners and for other heating purposes the unenriched, blue-flame water gas furnishes a clean, convenient fuel.

341. Producer gas, containing carbon monoxide as its essential constituent, is an important and cheap industrial fuel, because it can be made from low-grade coal. It is made by forcing a carefully regulated supply of air through incandescent coal:

$$2\,C + O_2 \longrightarrow 2\,CO\uparrow$$

The gas contains, in addition to carbon monoxide, a large amount (63%) of nitrogen and a small amount of hydrocarbons obtained from the coal.

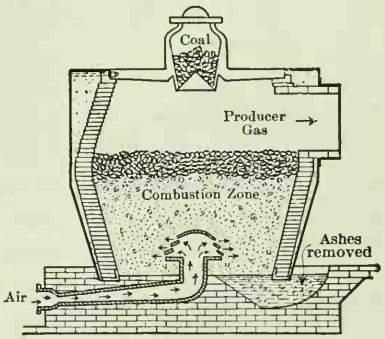


FIGURE 133.
Producer gas is made by blowing air in limited quantities through hot coal.

The generator, shown in Figure 133, resembles an ordinary stove in construction and operation. Carbon dioxide, formed at the bottom, is reduced to the monoxide while passing through the hot upper layers of coal.

Where soft coal is used, the heating of the coal in the upper part of the producer would add some coal gas, enriching the mixture to this extent. In some cases, steam is blown in with the air, and a product is obtained which contains a small amount of hydrogen.

Producer gas is often obtained as a by-product from blast and other furnaces, and its use is a considerable factor in the economy of the plant.

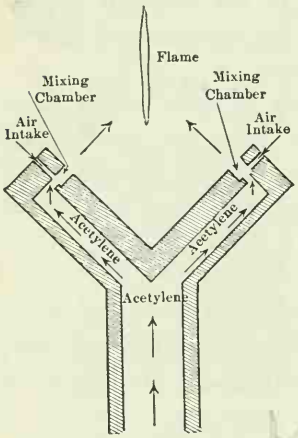


FIGURE 134.

This construction is necessary in order to secure enough oxygen to supply the flame. The two jets impinge in the middle and a flat, fan-shaped flame is formed in a plane at right angles to the plane of the paper.

342. Acetylene. — This gas serves remarkably well as a fuel gas in certain special cases. It is produced by the action of calcium carbide with water at ordinary temperatures.

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2\uparrow + Ca(OH)_2\downarrow$$

Acetylene is thus produced in automatic generators where the water is allowed to remain in contact with the carbide only so long as is necessary to produce the gas steadily and as fast as the use demands. The facts that its production is thus easily controlled and that, when burned in burners of special construction (Fig. 134), it produces a flame of dazzling brilliancy, make acetylene suitable as an illuminant for houses that are removed from a central lighting supply. Some danger attends its use because it forms explosive mixtures with air in which the air may vary considerably in its pro-

portions. This is partly offset by the fact that its distinctive odor reveals its presence in case of leaks.

When an acetylene flame is fed with oxygen instead of air, a temperature of 4000° C. is obtained. Heavy steel plates and beams are readily cut by the use of the oxy-acetylene cutting blowpipe shown in Figure 135. A simpler form of blowpipe which delivers a single jet of a properly proportioned mixture of oxygen and acetylene is used in mending broken or defective castings. This process, called *autogenous welding*, is a way of soldering with iron. The blowpipe is used to melt the edges to be joined, and at the same time a stick of iron or steel of the same composition is melted by the blowpipe and the melted metal runs into the gap.

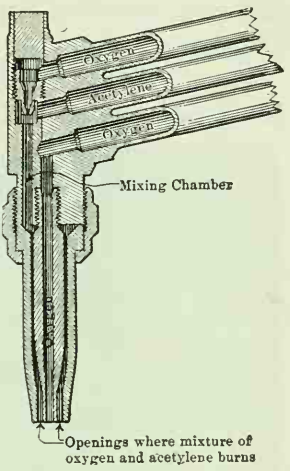


FIGURE 135.

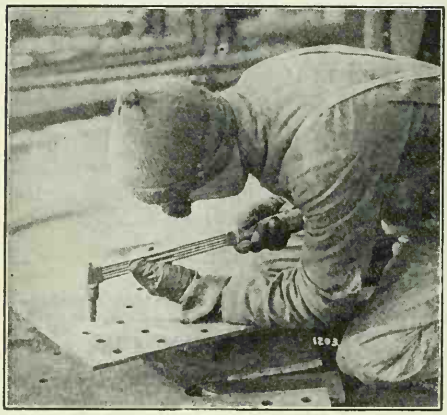
By this device a heavy steel beam can be cut. Six small flames of oxy-acetylene mixture surround a central tube which furnishes oxygen. The flames heat the steel to a high temperature and the central oxygen jet burns away a small strip of the metal.

343. Liquid fuels are more easily stored or transported than gas or coal. The alcohols, ethyl alcohol (C_2H_5OH) and wood alcohol (CH_3OH), are rather costly for fuel, but are desirable for use in small stoves and heaters, as they burn with clean, hot flames. The chief liquid fuels, however, are obtained from petroleum.

344. Petroleum is an inflammable, oily liquid, obtained from the earth, and consisting essentially of mixtures of many

different hydrocarbons, which are compounds containing only the elements carbon and hydrogen. It occurs in widely distributed natural reservoirs that are covered by impervious rock and filled with sand or other porous rock material that serves as a sponge to hold the oil (Fig. 137).

The distillation of petroleum furnishes several valuable liquid fuels, especially gasoline and kerosene. *Fractional distillation* is the separation of a mixture into parts (fractions) differing in their boiling points, by distilling the mixture and collecting separately parts of the distillate.



Courtesy of the Oxweld Acetylene Co.

FIGURE 136.

The blowpipe shown in Figure 135 is being used to burn away steel in order to make rivet holes in a steel plate.

Petroleum may be separated into useful substances by fractional distillation, but oil refiners generally combine fractional distillation with a kind of destructive distillation. As the distillation of the petroleum proceeds, the boiling point of the liquid in the still rises. A portion of the vapor that condenses is made to drop into the hot oil remaining in the still, and at once becomes superheated and decomposes, yielding other compounds having a lower boiling point. The decomposition of the higher hydrocarbon compounds of the oil is termed *cracking*.

A diagram of a petroleum still is shown in Figure 138. The distillate from the crude oil is separated into three fractions. This is accomplished by two air-cooled condensers, *B* and *C*, from which the successive fractions pass through three coils of pipe immersed in a tank of water, D. The fractions thus condensed are run into different storage tanks by means of

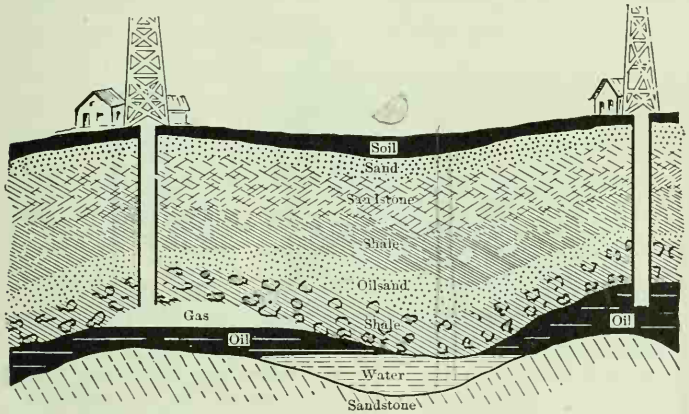


FIGURE 137.

Showing how petroleum, natural gas, and water may be contained in the strata of rock underground. If you drove a well in the middle you would get only salt water. In the two positions shown you would get gas and petroleum respectively.

a distributing sink, *E*. The process of distillation may be continued until only coke is left in the still.

Each of the three fractions obtained by the distillation of the crude oil is redistilled and otherwise treated to obtain from it substances for which there is a demand. Gasoline, benzine, kerosene, gas oils, lubricating oils, vaseline, and paraffin are a few of the many products obtained from petroleum. Paraffin is separated from a fraction of one of the petroleum distillates by artificial chilling.

The great demand for gasoline for use in automobile and other internal combustion engines has been the cause of much research on the cracking of hydrocarbons. Processes for cracking petroleum distillates heavier than gasoline have been developed and the products, known as cracked or artificial gasoline, have greatly augmented the natural

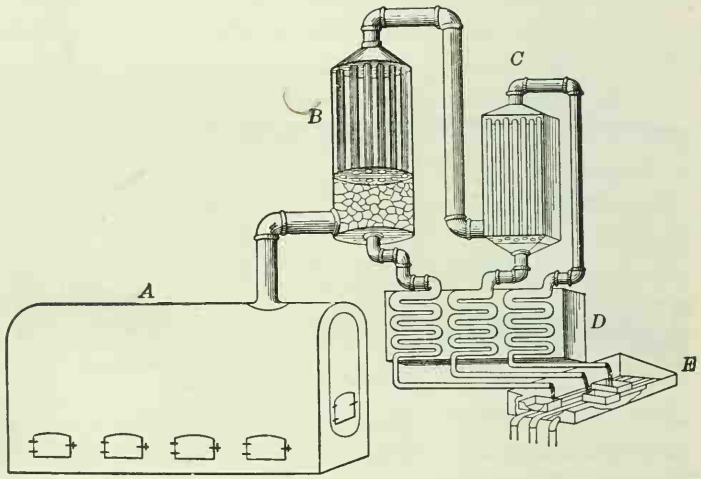


FIGURE 138.

Three products of different degrees of volatility are separated at the same time in this apparatus for the destructive distillation of crude petroleum

gasoline produced by the fractional distillation of petroleum. Increasing the yield of gasoline, however, necessarily decreases the yield of kerosene and heavier oil.

Gasoline evaporates rapidly, furnishing a combustible vapor. Kerosene is somewhat heavier and is slower in evaporating. The kerosene lamp has a wick to lead the kerosene into the hot flame where it can evaporate and take fire. Gasoline does not need a wick.

The petroleum fuels, like the petroleum itself, are mixtures of hydrocarbons in very variable proportions. As fuels, they are more convenient and efficient in use than coal, and a pound of kerosene will give as much heat as $1\frac{1}{2}$ pounds of good coal.

345. Flame of Candle. — We have seen numerous cases of combustion or burning. When the fuel is a solid, particles of the fuel or of the ash are often heated to incandescence and glow. When a stream of gas burns, a flame is produced. This phenomenon can best be studied in the flame of a common candle (Fig. 140).

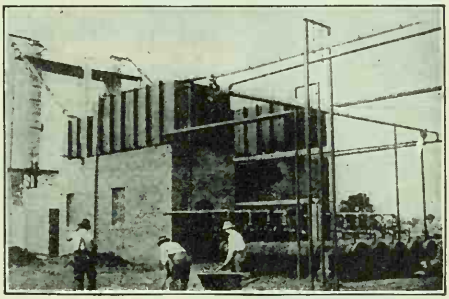


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FIGURE 139.

In this still gasoline is separated from its less volatile constituents.

Starting about one eighth of an inch from the candle, the flame begins to be visible, rounded at the base and tapering to a sharp point above. It entirely incloses the wick except at the base and at the extreme tip.

If we examine the flame closely, we see four parts. The first is a *greenish blue portion of the base*, shaped much like the cup of an acorn. Second, above and within the first green portion we find, immediately surrounding the wick, a region dark compared with the more brilliant part above, but in reality transparent and colorless, as is shown by placing an object behind it. This region tapers to a point above and

is termed the *non-luminous cone.* Covering the cone just mentioned is a bright cap known as the *luminous cone.* This is the third and most conspicuous region of the flame. Outside the luminous cone we can find the fourth region, which is the faint and scarcely visible blue *mantle.*

FIGURE 140.

There are four distinct parts or zones in a luminous flame.

The candle is composed of a mixture of paraffin and stearic acid, both of which contain carbon and hydrogen. The upper portion of the candle, heated by the flame above, melts, so that the top becomes a cup holding a small portion of the melted fuel. This melted portion is drawn up the wick by capillarity, and, vaporizing, forms the non-luminous cone immediately surrounding the wick. If we insert a tube into this portion of the flame, we can lead out a quantity of vapor which condenses to a solid similar to that composing the candle. If we extend a thin piece of wire across the flame, we find that it is not very warm near the wick; in fact, the head of a match can be placed there without igniting. There is no combustion in this non-luminous cone since there is no air.

If we place a piece of cold porcelain in the luminous portion of the flame, or lead off some of the materials through a tube, we find a considerable portion of lampblack (carbon) and moisture. The carbon while in the luminous cone is heated to incandescence.

Since the combustible vapors are slowly mixed with air, the materials may move considerable distances from the

wick before they meet sufficient oxygen to burn. In the outer portion of the flame, the conditions are reversed, in that the air is in excess. Here the combustion is complete, but usually only a small amount of combustible material reaches this pale outer portion. This material, if drawn out by a tube, is found to be principally air mixed with products of combustion. The pale green cup below is similarly constituted; but because of its position *below* the principal region of combustion and its nearness to the cool wick and candle, it is not so warm as the blue mantle above.

The wick is made of cotton and is proportioned to the quantity of material to be burned. The cool stream of liquid drawn up the wick protects it from burning, and, at the same time, prevents the flame extending down to the candle. As the candle material is vaporized, the wick chars somewhat but does not burn, since there is no oxygen in its immediate vicinity. In braiding the wick, one of the threads is drawn tighter than the others, so that the wick, when free from the candle-stuff, is drawn over to one side of the flame. This braiding of the wick brings the tip into the outer zone of combustion, where it burns so far as air is available, rotating as the candle shortens and practically maintaining a uniform length. This is why modern candles do not need to be trimmed.

346. Gas Flames. — In the ordinary gas flame (Fig. 141), as well as in the candle flame, the four regions are clearly marked: the region of fuel, or non-luminous cone; the luminous cone, or region of luminosity; outside and lower regions of combustion with an excess of air. The size and shape of gas flames depend largely on the *tip* of the burner.

In a bunsen burner (§ 29), we can adjust the proportions of gas and air so that there shall be no excess of either. Then the flame will appear to have two regions, a lower cone where no combustion is apparent, and the cap above.

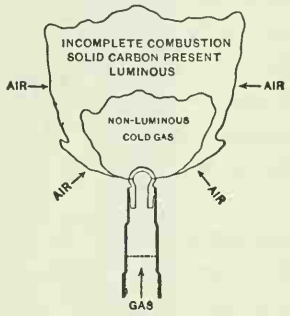


FIGURE 141.

It is fine particles of heated solid carbon that make this type of flame luminous.

In the bunsen flame, we find the position of maximum temperature somewhat above and outside the inner cone. A very large part of the energy passes off as heat and only a very small per cent is converted into light. If the solids giving light could be placed above or in the region of maximum temperature, they would evidently be hotter and give more light. Auer von Welsbach accomplished this by placing a mantle composed of a net of infusible and incombustible materials in the outer portion of the flame of a bunsen burner. The materials are heated to incandescence and produce the brilliant light given by the Welsbach burner.

347. Explosive Mixtures. — Mixtures of air with gaseous fuels or with the vapors of liquid fuels burn with great rapidity because of the intimate association of the combustible and oxygen. When the combustion is very rapid, such a mixture is called an *explosive mixture*. The rapidity of the burning depends upon the relative proportions of gaseous fuel and air. *The range of explosive mixtures for a given fuel extends from the mixture containing the least percentage of the gas and the highest percentage of air that will burn explosively*

to that containing the highest percentage of gas and the least percentage of air that will so burn. The extent of this range varies considerably with different fuel gases. For any particular gas, there is a definite mixture of greatest explosive power.

Since such substances as gasoline, benzine, and naphtha evaporate rapidly when exposed to air, an open flame should never be brought into the vicinity of these liquids, as any explosive mixture of their vapor and air is likely to be ignited. Explosive mixtures, on the other hand, are the source of power in internal combustion engines, such as the gas engine and the automobile engine. Here the terms "lean" and "rich" mixtures are used to indicate respectively a low or a high proportion of the gaseous fuel. Because of slower evaporation, richer mixtures are used in cold than in warm weather.

SUMMARY

Coal gas is produced by the destructive distillation of soft coal.

A destructive distillation is the process of decomposing complex organic substances by heat in closed vessels, and condensing the vapor of the liquid products.

Ammonia, coal tar, and **coke** are also obtained by the destructive distillation of soft coal.

Water gas is obtained by the reaction of steam with incandescent coal. For illuminating purposes, it is enriched by the addition of gases obtained by the decomposition of petroleum oils or by the addition of benzene.

Water gas contains carbon monoxide, hydrogen, and hydrocarbons.

Producer gas, used only as a fuel, is made by the action of air, sometimes mixed with a small amount of steam, on incandescent

coal. Its active constituents are carbon monoxide and small amounts of hydrogen and hydrocarbons. A large amount of inert nitrogen remains in the gas.

Acetylene is a gas of high illuminating power, made by the reaction of calcium carbide with water.

Gasoline and **kerosene**, the most common liquid fuels, are obtained from petroleum by fractional distillation and by cracking higher hydrocarbons.

Fractional distillation is the separation of a mixture into fractions, differing in their boiling points, by distilling the mixture and collecting separately parts of the distillate.

Gasoline evaporates rapidly at the ordinary temperature, giving a vapor that burns readily.

Kerosene in lamps and stoves is fed generally by a wick, into the hot flame, where it evaporates and takes fire.

The candle flame shows four distinct regions: the green-blue part at the base where little burning is taking place; the non-luminous central cone of combustible vapor about the wick; the luminous mantle; and the blue outer mantle where the burning is completed.

The bunsen flame shows two distinct regions: the inner relatively cool cone, and the blue outer mantle, which is hotter.

The ordinary gas and kerosene flames have four parts similar to the candle flame.

Explosive mixtures of a combustible gas (or vapor) and air are mixtures that burn very rapidly. Their range of composition varies greatly with the kind of gas or vapor burned. They are a source of danger in the home and laboratory, but are used for power in automobile and gas engines.

EXERCISES

1. What is meant by destructive distillation?

2. Mention important substances resulting from the destructive distillation of soft coal.

3. Give the important steps in the manufacture of illuminating gas from soft coal.

4. Mention four important products obtained during the manufacture of illuminating gas from soft coal.

5. Calculate the weight of steam that could be decomposed by a ton of incandescent coke containing 90% carbon.

6. Show that it is economical to manufacture coal gas and water gas in the same plant.

7. Which is better adapted for manufacturing purposes, producer gas or unenriched water gas? Explain.

8. What is fractional distillation?

9. What advantages are secured by the use of petroleum as a fuel in steamships?

10. What is meant by the " cracking " of oils?

11. By what means has the production of gasoline been increased?

12. What is the advantage of gasoline over kerosene for use in automobile engines?

13. What are the products of the combustion of gasoline?

14. Indicate by a diagram the principal parts of a candle flame. Compare these parts with respect to temperature and light-producing properties. Why is a flame extinguished by surrounding it with carbon dioxide?

15. Why is the flame of a bunsen burner hotter with the holes open than when they are closed? Is the total heat increased?

16. Why does not the flame of a bunsen burner extend down the tube to the base?

17. If a taper is held over a gas burner, a flame may some-

times be maintained several inches above the burner without "striking back" to the burner. Explain.

18. Why is carbon more likely to form in an automobile cylinder in cold weather than in summer?

19. Why should cleaning with gasoline never be done indoors after dark?

20. How many cubic feet of air are necessary for the complete combustion of 750 cu. ft. of methane?

21. Why is a Welsbach burner provided with a chimney?

22. State what is accomplished in the *carburetor* and in the *superheater* of a water gas plant.

23. (*a*) Calculate the per cent of carbon in acetylene.
(*b*) Why does acetylene give such a bright flame when used in a burner of special construction?

24. How is the necessary heat produced for the oxy-acetylene cutting of steel? What happens to the steel along the line of the cut?

25. Describe how a broken iron casting could be mended with an oxy-acetylene flame. What is the process called?

CHAPTER XXVI

COLLOIDS

348. Crystalloids and Colloids. — The subject of colloids deals with mixtures that seem to be solutions, but which, in reality, are suspensions of matter in a state of division that is intermediate between the extremely minute particles of true solutions and the larger aggregations that settle on standing. The first realization of this condition occurred about sixty years ago when Graham discovered that certain apparently dissolved substances, of which gelatin, albumin in the white of egg, soap, cooked starch, rubber, and cement are good examples, pass through membranes very much more slowly than do water solutions of ordinary acids, bases, and salts. Hence substances were divided by Graham into two classes: *colloids*, which do not diffuse, or dialyze, readily through membranes, and *crystalloids*, which do.

In explanation of these facts, it was supposed that crystalloids are suspended in the form of extremely minute particles, and that colloids exist in their apparent solutions as aggregations so large that they cannot get through the small pores of animal membranes.

349. The Ultramicroscope. — Zsigmondy, in studying the coloring effect produced by mixing metallic gold with glass, tried to extend the range of vision of the microscope. He sought to produce the Tyndall effect in the field of the instrument. This is what we observe when a beam of sunlight

enters a partly darkened room and makes visible the suspended dust particles that cannot ordinarily be seen. Zsigmondy caused intensely concentrated rays from an arc lamp or the sun to pass at right angles through the completely darkened field of a microscope. He discovered that gold in glass could be distinguished as separate particles, so small that they cannot be seen in the ordinary microscope, but still large in comparison with atoms and molecules. The invention was named the *ultramicroscope.*

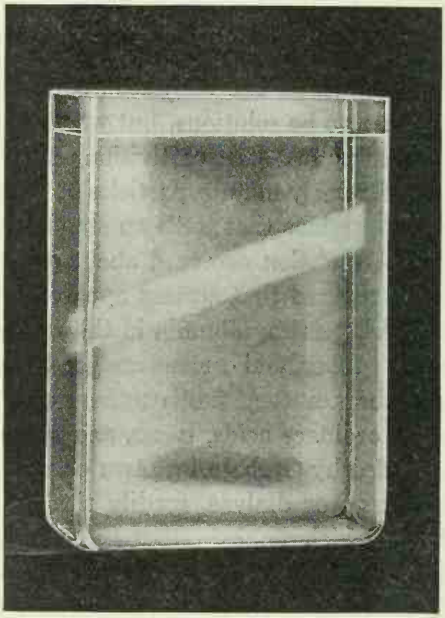


FIGURE 142.
A strong beam of light reveals the presence of colloidal particles in the solution.

It occurred to Zsigmondy that he might discover something about colloids by studying them with the aid of his new invention He and others have shown that a knowledge of colloids interprets for us some of the common and important matters of practical life, such as the cleansing action of soap, the setting of jellies, the formation of deltas in rivers, and many other things.

350. Main Characteristics of Colloidal Particles. — It was found that the particles of dispersed (suspended) colloids

could be seen in the ultramicroscope. It was found that they are prevented from settling by a vibratory motion, plainly visible in the ultramicroscope, that is known as the *Brownian movement* (Fig. 143). Dispersions of coarse particles do not show this motion. The reason is probably as follows: the molecules of liquids do not move with equal velocities; a particle suspended in a liquid may, therefore, be unequally bombarded on its opposite sides by the moving molecules of the liquid; if the suspended particle is relatively large, the inequality of the bombardment will be negligible in comparison with the mass of the particle, and nothing will happen; but if the suspended particle is small, the unequal blows of the liquid molecules will be sufficient to set it in motion. So dispersions of *fine* particles will not settle because they are thrown into Brownian movement. This motion is the most characteristic thing about colloids. Any substance can be put in the colloidal condition by producing particles that are small enough to experience the Brownian movement. Since such suspensions have a definite set of properties, different from those of true solutions on the one hand, and from those of true suspensions, on the other, we have a special aspect of mixtures that is known as the colloidal condition.

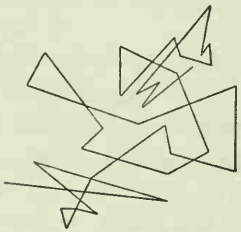


FIGURE 143.

The path of a colloidal particle. An ultramicroscope thus shows us the results of the collisions and bombardments that occur within the solution.

Many colloids have the power of taking up the liquid in which they are suspended. The swelling that occurs when gelatin is soaked in water is a good illustration of this property. In the case of colloids, however, this adsorption does

not follow the law of definite proportions, as some crystal compounds do when they unite with water of crystallization.

Unlike solutions, colloids reveal the path of a beam of light that passes through them, because the particles are large enough to reflect the rays of light that strike them. This is shown in Figure 142.

Colloidal particles bear electric charges, some positive, some negative. Most colloids are negatively charged when suspended in water.

351. Colloids show osmotic pressure, but only in a degree that is small in comparison with that of true solutions. This is due to the fact that Brownian movement is slow in comparison with that of ions and molecules.

352. Sols. — Liquid mixtures that contain colloidal particles in suspension are called *sols*. This name serves to distinguish them from true solutions, with which they were formerly confused.

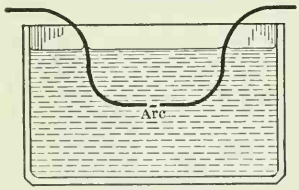


FIGURE 144.

The particles of metal that are torn away from the wires in the process of forming an electric arc may be afterwards distributed through the liquid in the form of colloidal suspension.

353. Means of Producing Sols. — Typical colloids, such as glue, gelatin, and cooked starch, always show colloidal character when dispersed in a liquid. This is probably due to the fact that their molecules are very large; in other words, they are of colloidal dimensions. Other substances are obtained as colloidal suspensions (sols) only by using special means to obtain groups of molecules that are large enough to show the characteristics of the condition and yet small enough to be thrown into

Brownian movement by the action of the molecules of the medium in which they are suspended.

Special conditions of precipitation will cause many insoluble substances, notably ferric hydroxide, arsenic sulphide, and chromic oxide to form as sols.

An electric arc formed under water between silver terminals will produce a sol of silver (Fig. 144). Other metals can be used to give similar suspensions. Mechanical pulverization has also been used to produce particles small enough to remain in permanent colloidal suspension.

354. Zsigmondy's Table. — The accompanying diagram, adapted from Zsigmondy, shows the relation of size of particle to certain properties, and to our classification of dispersed systems into true solution, colloidal condition, and true suspension.

<table>
<tr><td colspan="4">Diameter of Particles in Millimeters
$\frac{1}{10000000}$ $\frac{1}{1000000}$ $\frac{1}{100000}$ $\frac{1}{10000}$ $\frac{1}{1000}$ $\frac{1}{100}$ $\frac{1}{10}$ 1</td></tr>
<tr><td colspan="2">Brownian Movement
Very Rapid</td><td>Brownian Movement
Slow</td><td>Brownian Movement
None</td></tr>
<tr><td colspan="3">Particles pass through filter paper.</td><td>Particles do not pass through filter paper.</td></tr>
<tr><td colspan="2">Oil emulsions in water do not form a separate layer.</td><td colspan="2">Oil emulsions separate.</td></tr>
<tr><td colspan="2">Quartz in solution does not form a sediment.</td><td colspan="2">Quartz solutions form a sediment.</td></tr>
<tr><td colspan="2">Visible only with the ultramicroscope.</td><td colspan="2">Visible with the microscope or with the naked eye.</td></tr>
<tr><td>Crystalloid solutions</td><td>Colloidal condition</td><td colspan="2">Suspensions</td></tr>
<tr><td colspan="4">Turbidities</td></tr>
</table>

355. Gels. — Sols on cooling, or sometimes on being heated, *set* to form a jelly-like mass, as, for example, when a gelatin dessert cools in the refrigerator, or when an egg is boiled. In this act, the colloidal particles of gelatin first unite with water and then join with each other to form a microscopic sponge-like structure throughout the mixture. Large quantities of water are held in the cellular spaces of the structure. In this way a small quantity of gelatin can give to a large quantity of water a semi-solid appearance. The name of *gel* is given a sol that has set in this way. Gels are frequently turned back into sols by application of heat, or by addition of even small quantities of foreign substances. Gels are common in both animal and plant structures.

356. Protective Colloids. — Milk is a colloidal suspension of albumin and casein. When a little acid is added the milk curdles; this means that the colloidal particles are thrown into larger aggregations that settle. If a colloid like gum arabic or gelatin is added to the milk, curdling does not readily occur, and the gum arabic or gelatin is said to have acted as a *protective colloid*. Lactalbumin, always present in milk, acts in this way. Mothers' milk is especially rich in this natural protective colloid.

357. Colloidal Suspension in Media Other Than Liquids. — So far we have been speaking as if liquids were the only means of holding suspended particles in colloidal dispersion. But as with ordinary solutions, the medium may also be either a gas or a solid. The following kinds of colloidal dispersions are common: (*a*) solids in gases; the red color of sunsets is due to the colloidal dust in the atmosphere;

(*b*) liquid droplets in gases, as in fogs; (*c*) liquid droplets in liquids, as in emulsions of oil and water; (*d*) solids in solids, as in the case of colloidal gold which imparts to glass a ruby red color.

358. Other Practical Aspects of Colloids. — Sols are even more common than true solutions. Milk contains albumin and casein in colloidal condition. All the cells of the body are composed mainly of colloids. Adhesive substances such as paste, glue, and asphalt owe their characteristic property to the fact that their colloid particles have a total surface area that is exceedingly great. Some of these applications will be taken up in detail.

Adsorbing Power of Colloids. — Most cases of adsorption (§ 317) are due to colloidal action of the kind that we have just mentioned in the case of adhesion. Many dyes are colloids that attach themselves to fibers in this way. The decolorizing effect of animal charcoal is a case of colloidal adsorption.

Swellings in the Body. — The tendency of albumins to adsorb water is increased by the presence of acids. If we prick a piece of gelatin with a needle that has been dipped in formic acid, a local swelling occurs that resembles the swelling that results from the bite of an insect; this result is exactly analogous to what happens when we are bitten by insects. In some diseases, organs swell from the colloidal adsorption of water.

Cleansing Action of Soap. — This is a somewhat complex matter. If the dirt is held in place by grease, the emulsifying power of soap is first called into play as a means of removing grease. But dirt that sticks even

when no grease is present is also removed by soap. In this case, soap breaks up the particles of dirt and then acts as a protective colloid in preventing their adhering to each other, or to the material that is being washed. It may also colloidally adsorb the dirt particles to itself.

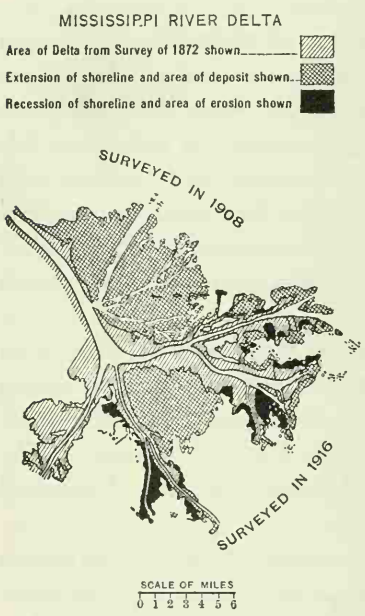


FIGURE 145.

Showing how rapidly deltas may be built as a result of the precipitation of colloidally suspended clay.

Formation of Deltas. — The very fine clay that rivers carry is suspended as negatively charged colloidal particles. When the river enters the ocean, the positive charges of sodium and magnesium ions that are present in salt water attract and neutralize the charge of the clay particles, which are then thrown out of colloidal condition and precipitated. The accumulation of this precipitated clay forms the delta (Fig. 145).

Colloidal Graphite. — The fine graphite that is used in making the lubricants known as aquadag and oildag is produced by treating mechanically ground graphite with gallotannic acid. This acts as a protective colloid, scattering the large graphite particles into colloidal dispersions that remain permanently suspended in oil or water (Fig. 146).

Mayonnaise. — The yolk of egg is a colloid that has the

power to adsorb large quantities of oil and vinegar. The colloidal emulsion that results is known as mayonnaise.

359. Photography. — The sensitive material of the photographic plate is composed of the colloid gelatin mixed with silver salts in the colloidal condition. The invisible effect that is produced by light during the brief exposure is probably adsorption of a minute quantity of metallic silver by the colloidal silver salt. In the finished negative we have colloidal silver held in gelatin.

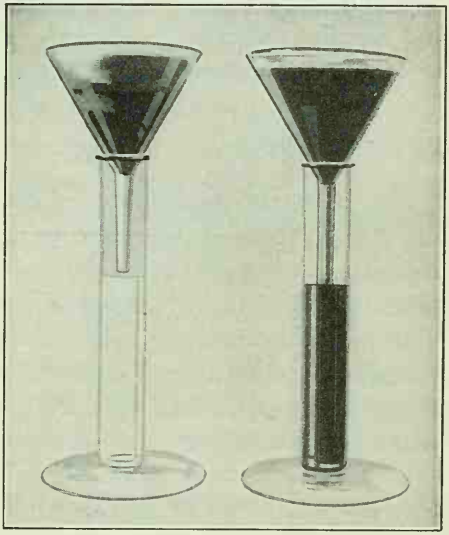


FIGURE 146.

In the first case graphite is suspended in the form of particles too coarse to pass through the filter paper. In the other case a deflocculating agent has been used and a colloidal suspension of graphite has resulted. The graphite in this case readily passes through the pores of the paper.

360. Cement, Mortar, and Plaster. — The freshly mixed mass contains gels made up of colloidal substances, such as calcium hydroxide, holding water within their structure. In the final setting, these colloids coagulate into larger aggregations of molecules that, in the case of cement, entangle crystalline substances produced by the absorption of water of crystallization from the gels.

361. Tanning. — Skins of animals consist of colloids. In the soaking operations that precede tanning proper, the skins adsorb water and form gels. Tannin and the other substances that produce the tanning effect are also colloids. The colloidal particles of the hides are positively charged, the tannin is negatively charged. Hence the two colloids are mutually attracted to and coagulated by each other. This change is followed by true chemical action that completes the process.

362. Soils and Agriculture. — The productiveness of soil depends not only on the presence of the necessary mineral constituents, but also upon the state of division of the soil particles. A soil is required that is porous enough to retain a considerable moisture content, and that has adsorbing power, dependent upon its colloidal condition, which is sufficient for the processes that are a part of all animal and plant growth. These conditions are best fulfilled when the soil particles are very small. It is a well-known fact that clay which is devoid of the vegetable débris known as humus will not raise crops. The explanation is that the decaying vegetable matter produces organic colloids that act protectively on the clay in the way that gallotannic acid does on graphite, breaking it up into particles that are of colloidal dimensions.

It has been observed that ordinary salt, or too great concentration of fertilizing material, destroys the productiveness of soils. The reason is partly that the electric charges of the ionized salts neutralize the colloidal charges of the clay particles and cause these to coagulate.

SUMMARY

Colloidal condition exists when suspended particles have dimensions larger than those of the solutes of true solutions and smaller than those of suspensions that settle on standing. The ultramicroscope shows colloids existing as separate particles, whose dimensions range from about $\frac{1}{100{,}000{,}000}$ to $\frac{1}{10{,}000}$ of a millimeter.

The Brownian movement that is shown by all particles in a state of colloidal suspension explains why these do not settle.

Colloids generally have a marked power to **adsorb** other substances. They are **electrically charged.**

Glue, gelatin, rubber, gums, and most animal and vegetable substances are natural colloids. Any substance, however can be obtained in the colloidal condition by producing particles small enough to have Brownian movement.

Sols are liquids that contain dispersed colloids.

Gels are semi-solid mixtures like ordinary jellies. They contain colloids which have adsorbed some of the suspending medium and formed a sponge-like structure whose cells are filled with additional quantities of the suspending medium.

Protective colloids tend to prevent other colloids from coagulating.

EXERCISES

1. State three important characteristics that are shown by particles when they are in the state of colloidal dispersion.

2. Distinguish between colloids and crystalloids.

3. What is meant by the term "Brownian movement"? Explain the cause of this movement.

4. Name three substances that always show colloidal characteristics when suspended in liquids. What are some of the ways that can be used to obtain other substances in the colloidal condition?

5. Why does the addition of electrolytes tend to precipitate

substances from the colloidal state? Give two practical examples of such precipitation.

6. The addition of dilute acid causes milk to curdle. Explain this fact.

7. Gum arabic is sometimes added to cow's milk used in feeding infants. What benefit results from this addition?

8. Explain why the particles of a colloidal suspension do not settle on standing.

9. Give examples of the following types of colloidal suspension: a liquid in a gas; a liquid in a liquid; a solid in a solid.

10. Strong acids tend to precipitate colloidal arsenious sulphide. Explain this fact.

11. In which of the following cases is a delta more apt to form: (*a*) when a muddy river flows into a fresh water lake, or (*b*) when such a river enters the ocean? Explain.

12. What is meant by the term "protective colloid"?

13. What experiment could you perform to show that, under certain circumstances, the saying "oil and water do not mix" is untrue?

14. What is meant by the term "adsorb"?

15. Cite facts that indicate that colloids generally have adsorbing power. Explain.

16. Describe the formation of a gel and explain its structure.

17. In making one kind of opaque water color paint, linseed oil is held in permanent suspension with water by the use of yolk of egg. Explain this fact.

18. Show the relation between the "sticky" qualities of adhesives and the fact that these substances are generally colloids.

19. Explain: swellings that result from insect bites; the curdling that accompanies the souring of milk; the cleansing action of soap; the importance of organic matter in farm soils; why a small quantity of gelatin makes a large quantity of dessert.

CHAPTER XXVII

SILICON AND BORON

363. Silicon. — Silicon, next to oxygen, is the most abundant element in the earth's crust. Nearly all the common rocks are silicon compounds. Silicon, as an element, is of comparatively little practical importance. A small percentage of silicon is found in cast iron and traces of it are found in steel. It is used as a detector in wireless telegraphy and in purifying iron.

364. Varieties of Silicon Dioxide. — Silicon dioxide, or *silica*, SiO_2, is the most common compound of silicon. It

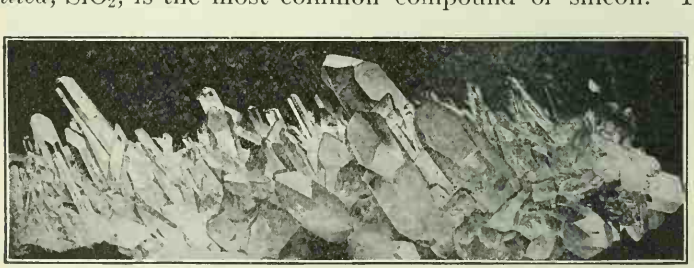


FIGURE 147.

Quartz is a naturally occurring crystalline form of silicon dioxide.

is found in many varieties, which differ in color and structure, owing to minute quantities of impurities, and to conditions under which they are formed. Quartz, the most common form, crystallizes in hexagonal prisms, surmounted by a pyramid (Fig. 147). Clear crystalline varieties are

known as rock crystal; purple varieties as amethyst. Rose quartz, milky quartz, and smoky quartz, or cairngorm stone, are varieties of silicon dioxide, colored by minute quantities of impurities. Onyx, agate, jasper, and flint are other forms of silicon dioxide. Opal is a hydrated form.

The shells of some microscopic organisms are composed of silicon dioxide, and infusorial earth is a deposit of these (Fig. 148). Sand is water-worn silicon dioxide, and sandstone consists of particles of sand cemented together.

FIGURE 148.

Shells of minute sea animals as seen under the microscope. They consist of silicon dioxide.

Silica is found in most plants, especially in their stalks and stems. It imparts firmness to the stems and to the resistant exterior coating of straws, scouring rushes, and bamboo. Sponges, the quills of feathers, claws of animals, and the finger nails contain considerable silica.

365. Properties of Silicon Dioxide. — Silica is harder than glass; it is insoluble in ordinary reagents, but will dissolve in melted alkalies.

366. Uses of Silicon Dioxide. — White sand, which is nearly pure silicon dioxide, is used in making glass and porcelain. Common sand is discolored by impurities, and if the particles are sufficiently irregular and angular it can be

used in sandpaper and mortar. Sandstone is used for building; hard varieties are used for grindstones and millstones. Ground glass is glass that has been roughened by blowing sand against it by means of a blast of air. Many clear varieties of quartz are cut and polished for jewelry, as amethyst, agate, carnelian, false topaz, and imitation diamond. Petrified wood has been formed by the gradual replacement of the woody fiber by silica, which preserves the woody appearance. Cut and polished petrified wood is used as an ornamental stone. The fine varieties of infusorial earth are used as abrasives in polishing powders, and are also used in cements, in refractory fire brick as a heat insulating material, and as an absorbent. Silicon dioxide is used as a filler in paint. Quartz, melted by the oxyhydrogen flame or the electric furnace, can be drawn into delicate elastic threads which are used in scientific instruments, and is fashioned into tubes and apparatus for use in the laboratory. This material is called *vitrified silica* (Fig. 149).

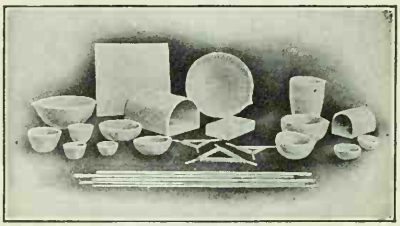


FIGURE 149.

The electric furnace gives a temperature sufficiently high to melt silicon dioxide. The articles thus made of melted sand resist sudden change of temperature much better than glass does. They will not melt or soften in ordinary flames.

367. Silicates.—Silicon dioxide reacts with the hydroxides of the alkali metals, sodium and potassium, to form silicates:

$$SiO_2 + 2\ KOH \longrightarrow K_2SiO_3 + H_2O$$

Sodium and potassium silicates are soluble in water; nearly all the other silicates are insoluble, stable com-

pounds, which comprise the larger part of the earth. Such minerals as feldspar, mica, hornblende, and clay are silicates. These are derived from complex silicic acids, of which silicon dioxide is the anhydride. Various mixtures of these comprise the common rocks, as granite, gneiss, and slate.

Sodium and potassium silicates are made by heating to fusion the metallic hydroxides, or carbonates, with silicon dioxide. The thick water solution, called *water glass*, is used in filling soaps, in sizing for walls, calico printing, preservation of eggs, and fireproofing wood and textiles.

Silicon dioxide is the anhydride of silicic acid:

$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$

At high temperatures, silicon dioxide combines directly with basic oxides, like calcium oxide (§ 414), to form silicates:

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

This action is the basis for the formation of *slag*, in the extraction of iron and other metals.

368. Glass. — The shutting off of supplies of glass from foreign countries during the war gave great impetus to the study and manufacture of glass in the United States. Before the war, large quantities of bottle, plate, and window glass were manufactured, but most of the chemical glassware, and practically all of the optical glass, were imported. This country was noted for its ornamental cut glass, Favreuil art glass, and railway signal glasses. War conditions were either directly responsible for, or greatly hastened, the manufacture of —

(*a*). glass that contained neither potassium nor lead, of excellent quality for making electric light bulbs:

(*b*) glasses of superior quality for chemical glassware;
(*c*) a remarkable glass for baking dishes;
(*d*) optical glasses.

Glass is an amorphous material, commonly made by the fusion of a mixture consisting of silicon dioxide, sodium carbonate, and either calcium carbonate or lead oxide. Com-

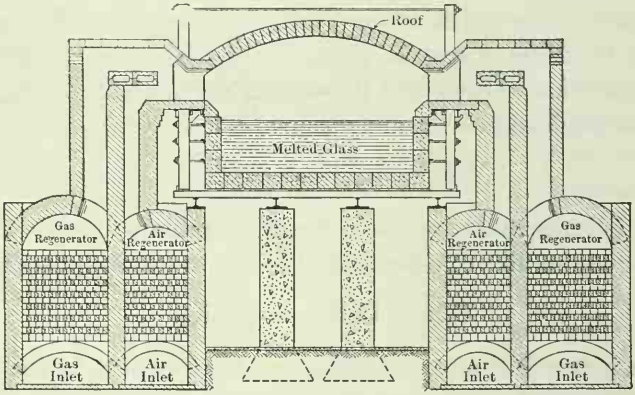


FIGURE 150.

This glass furnace maintains a high temperature economically. Producer gas is used as a fuel, and both it and the air needed for its combustion are preheated by being made to pass through regenerators before entering the furnace proper. Their direction of flow alternates at frequent intervals, and the brick checker-work of the regenerators is thus kept hot by the gaseous products of combustion as they escape from the furnace.

mon glass may be regarded as a mixture of silicates, or as a solid solution in which silicic acid acts as the solvent. In special glasses, borates and phosphates may be substituted for silicates, and compounds of zinc, barium, antimony, and other metallic elements may be used.

Transparent glasses are technically divided into *lime glasses* and *lead glasses*. Small quantities of iron are generally

present in the sand used in glass making, and if a ferrous compound be produced in the glass, it will impart a green color to the mass. To overcome this difficulty, some oxidizing agent, such as sodium nitrate or manganese dioxide, is used to convert the ferrous compound into a ferric compound, which at most will impart a light yellow color to the glass.

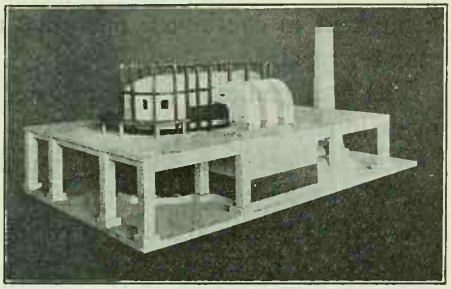


FIGURE 151.

This model of a modern glass furnace shows the furnace above, the regenerators below, and the large pipes that convey the preheated gases to the furnace.

Glass is manufactured in enormous tank furnaces (Figs. 150, 151, 152) divided into compartments by suitable obstructions, and heated by flames passing across above the charge in the furnace. The mixture of raw material is placed in one end of the furnace, where it is heated. Silicates are formed and carbon dioxide is evolved when the chemical changes are nearly complete. The glass is then gradually worked under the obstruc-

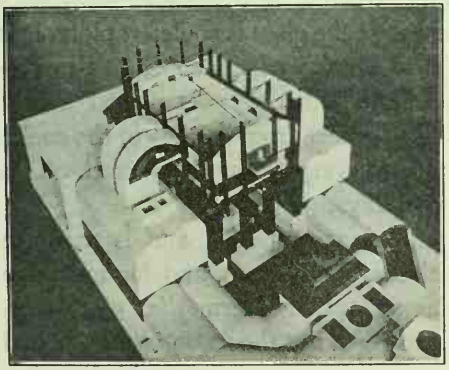


FIGURE 152.

Another view of a model of a glass furnace.

tions, and finally removed at the other end of the furnace. When a batch of glass is taken from the furnace, a batch of raw material is added at the other end, the furnace thus being kept in continuous operation until it is necessary to stop for repairs.

The finer grades of glass, for example, optical glasses, are made in clay melting pots.

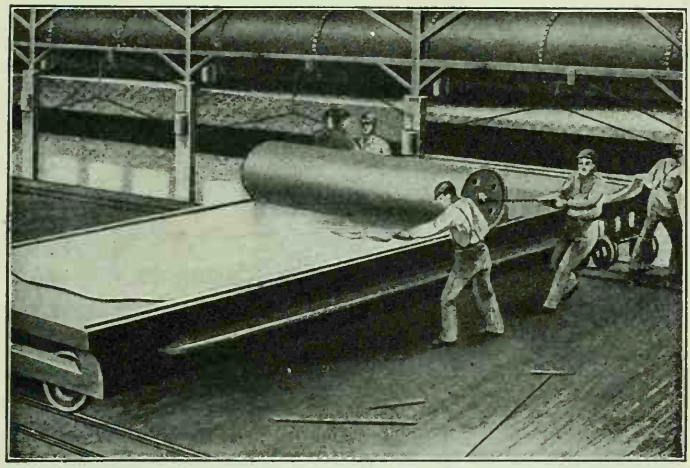
Window glass is a sodium-calcium glass. It is made by the workman taking a mass of the molten glass on the end of a long iron blowpipe, and blowing it into a large bubble. This is drawn out into a cylinder by swinging it and rolling it on a plate. The ends of the cylinder are cut off, a cut is made lengthwise, and the glass is spread out flat. Machinery has largely replaced hand work in manufacturing window glass. *Plate glass* is made by pouring the molten glass on a bronze table, rolling it with a hot iron cylinder (Fig. 153), and finally polishing it. *Crown glass* is a colorless window glass used for convex lenses.

Cheap glass dishes and similar objects are made by pressing the plastic glass in a die. Bottles are blown in a mold, often by a machine. If the glass is cooled rapidly, it is hard, brittle, and liable to break under a shock. To overcome this it is *annealed*, that is, the glass is passed slowly through a long, tunnel-like furnace from the hot to the cooler end, so that the temperature is very gradually lowered. This process often takes several days.

Flint glass is brilliant, heavy, and soft, and is used for concave lenses, lamp chimneys, cut glass, and for imitation gems, such as paste diamonds. The term *flint glass* originally meant a potash-lead glass, but the name is now applied to other glasses that are clear. *Cut glass* is lead or barium glass molded to the desired shape; the design is cut

by a wheel, and the glass polished with rouge or putty powder.

Glass is colored by dissolving various substances in the melted mass. The green color of common glass is due to iron compounds in the sand and calcium carbonate; chromium compounds give a rich green. Compounds of cobalt



By courtesy of The Scientific American.

FIGURE 153.

Plate glass is made by rolling the hot, plastic material on a bronze table.

give blue color; manganese, pink to violet; silver, yellow; calcium fluoride, white and translucent.

The color of ruby glass is due to colloidal particles of gold. *Pyrex glass* is a borate and silicate of aluminum. It is stronger and tougher than ordinary glasses, is not so quickly attacked by water and other solvents, and will stand considerable change in temperature without cracking. Selenium, in the colloidal condition, is used to produce a clear red glass of great value for railway signals.

369. Silicon Carbide or Carborundum. — Silicon carbide, or carborundum, is a crystallized solid, often brilliant and

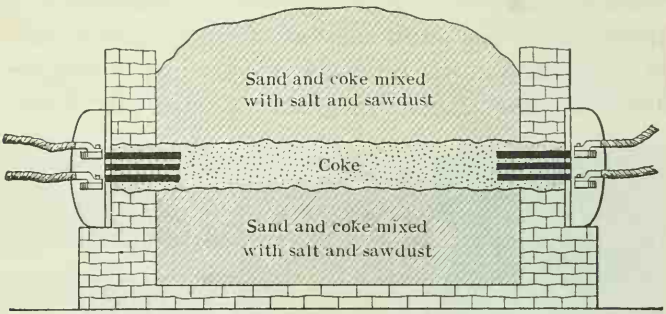


FIGURE 154. — A DIAGRAMMATIC REPRESENTATION OF A CARBORUNDUM FURNACE.

iridescent, and varying in color, a fact which is due to surface tarnish. It is extremely hard, and is used as a substitute

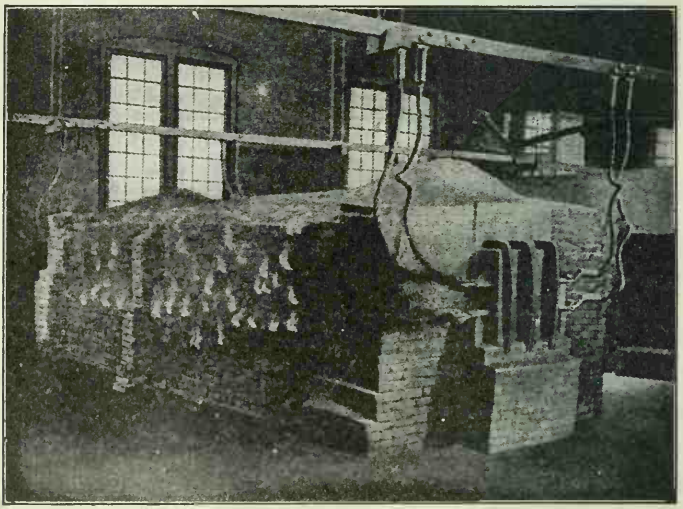


FIGURE 155. — A FURNACE FOR MAKING CARBORUNDUM.

for emery for grinding and polishing wheels, hones, and carborundum cloth (Fig. 156).

Carborundum is made in an oblong electric furnace, at the ends of which are metal plates to which are attached the heavy carbon electrodes projecting into the furnace (Figs. 154, 155). The electric connection between the electrodes is through a mass of granulated coke. The mixture to be melted is composed of coke, sand, sawdust, and a little salt. The salt is used to aid fusion, and the sawdust to make the mass porous. This mixture is piled around the central core of coke and held in place by side walls of loosely piled bricks (Fig. 155). The action in the furnace is not electrolytic, but is due to the heat generated through the resistance of the coke to the current. The carbon reacts with the melted sand to form carbon monoxide and carborundum:

FIGURE 156.

Carborundum as an abrasive. There is something here that can be used to sharpen almost any tool that is made.

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO$$

The action continues for about eight hours. When the furnace has cooled, the sides are torn down and the carborundum removed. The best crystals are found around the central core. The crystals are crushed, washed with sulphuric acid, dried, and graded according to size. They are used as powder, or cemented into wheels (Fig. 156).

370. Boron. — The element boron is of little importance. It is a brown powder, soluble in many melted metals, and infusible at the temperature of the electric arc. Its important compounds are boric acid and borax.

371. Boric acid, H_3BO_3, occurs in minute quantities in vapors arising from the earth in the volcanic regions of Tuscany, in Italy. The boric acid used in the United States is made by the reaction of calcium borate with sulphuric acid.

Boric acid is obtained in fine crystalline scales. It is a weak acid, sparingly soluble in cold water. It is used as a valuable and comparatively safe household antiseptic.

372. Borax. — The familiar compound, borax, is sodium tetraborate, $Na_2B_4O_7 \cdot 10\,H_2O$. In California there are large deposits of impure borax and calcium borate. Commercially, borax is prepared from calcium borate by reaction with sodium carbonate.

Borax is obtained from solutions in large crystals, containing 10 molecules of water of crystallization, $Na_2B_4O_7 \cdot 10\,H_2O$. A solution of borax has an alkaline reaction.

Borax is employed in large quantities as an antiseptic and as a cleansing agent. In soldering and welding, it is used to dissolve the metallic oxides formed by heating the metal.

Borax Bead Tests. — When heated, crystallized borax swells during the evaporation of the water of crystallization and then melts to a clear glassy mass. Fused borax dissolves metallic oxides, and these often impart to the glassy mass a color characteristic of the metal. Thus, when heated with a drop of fused borax in the oxidizing

flame, cobalt compounds give a blue color, and manganese compounds a violet color.

SUMMARY

Silicon is a very abundant element which, in itself, is of little practical importance. **Silicon dioxide** (silica) is its most common compound, occurring as quartz and sand, and as a constituent of many rocks.

Silicon dioxide is very hard and fuses only at high temperatures. It is used in making glass, mortar, and polishing powders.

Silicates are salts of silicic acids. Sodium and potassium silicates are soluble.

Glass is a mixture of silicates. Transparent glasses are generally lime glasses or lead glasses. The materials are melted together and blown or molded into shape while plastic. While in a melted state, compounds may be added to color the glass.

Silicon carbide is made by heating coke and sand in an electric furnace. It is used as an abrasive.

Boric acid is found in nature, but much of it is made from calcium borate.

Borax occurs in large deposits in California. It gives characteristic reactions with metallic oxides used in bead tests. Borax is also used in soldering and welding, and as a cleansing agent.

EXERCISES

1. Give the more important uses of silicon dioxide.

2. Why is sand the main final product of long-continued disintegration of rock materials by water?

3. What is water glass? How is it made, and what are some of its uses?

4. What is vitrified silica? Why should not basic substances be melted in silica ware?

5. Give the essential composition of a glass.

6. Describe the manufacture of glass.

7. Using an equation, explain the production of carbon dioxide in glass making, and state how it is eliminated.

8. How is glass annealed? What is the effect of this process on the properties of the glass?

9. Explain, with the aid of an equation, the action of hydrofluoric acid on glass.

10. What is carborundum? Write the equation for its preparation. What is its chief use?

11. Calculate the percentage of water of crystallization in borax.

12. Account for the color of the glass in (*a*) jars used for canning fruit, (*b*) railway danger signals.

13. What causes borax to swell when it is heated in the bunsen flame? What action has the fused mass with some metallic salts?

14. Sand and compressed air are used in a sand blast for cleaning castings. Why?

15. State briefly the differences in the making of ground glass, plate glass, and cut glass.

CHAPTER XXVIII

CALCIUM AND ITS COMPOUNDS

Calcium

Although metallic calcium has been known for many years, it is only recently that it has been made in any quantity. Sir Humphry Davy was the first to obtain the metal, but failed to get enough to determine its properties. The credit for the successful isolation of calcium belongs to Dr. Robert Hare, a scientist of Philadelphia. His electrolytic method, with some modifications, is the one now used to obtain the metal.

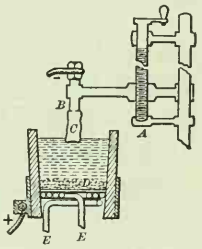


Figure 157.

This ingenious device for preparing calcium uses the growing stick of metallic calcium as the cathode. Calcium chloride is kept in a state of fusion by its resistance to the electric current. Too high a temperature is avoided by the coil of pipe through which cold water flows.

373. Preparation. — Metallic calcium is prepared by passing an electric current through fused calcium chloride contained in a crucible of graphite, which acts as the anode (Fig. 157). At first the cathode is an iron rod (*B*), capable of being raised by a screw mechanism (*A*). The calcium deposit on the end of the iron rod solidifies, and grows downward as an irregular cylinder. This rod of calcium becomes the cathode (*C*) as the iron rod is gradually raised out of the molten chloride by the screw mechanism. A coating of calcium chloride protects

the calcium from oxidation as it emerges from the molten bath. The electric current, by its passage, keeps the calcium chloride molten in the graphite crucible, except at the bottom (*D*), where it is kept cold and is solidified by water running through a copper coil (*EE*). The chloride adhering to the sticks of calcium is removed by hammering.

374. Physical Properties. — Pure calcium is a silver-white metal of brilliant luster, and is a little lighter than magnesium. It is harder than lead or tin, but softer than zinc.

375. Chemical Properties. — Calcium keeps its luster in dry air and can be preserved without difficulty in a stoppered bottle. In moist air its surface becomes dulled. Molten calcium burns vigorously in oxygen and in chlorine.

Water is *slowly* decomposed by calcium, and hydrogen is evolved at a rate very convenient for the collection of the gas:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

Calcium Carbonate

376. Occurrence. — Calcium carbonate, $CaCO_3$, is one of the most abundant compounds occurring in nature. In the form of limestone, it constitutes whole mountain ranges. Marble is a purer form of calcium carbonate than limestone. Marble was formed from limestone by the action of heat and pressure under such conditions that carbon dioxide, which generally is given off when limestone is heated, was prevented from making its escape.

The mineral matter in shells is chiefly calcium carbonate derived from the water in which the animals live.

In past ages, deposits of shells became cemented together into rock materials. Coquina, or the loose shell rock of Florida, illustrates an early stage of this process (Fig. 158), and limestone a more complete transformation.

Calcite is a pure crystalline form of calcium carbonate, and one of its varieties, Iceland spar, gives a double refraction of light (Fig. 159). Chalk is a fossil calcium carbonate, and dolomite is a double carbonate of calcium and magnesium.

FIGURE 158.

Coquina consists of small sea shells that have become cemented together. It is essentially calcium carbonate.

377. Properties. — When pure, calcium carbonate is a white solid, often transparent. The color of limestone and many varieties of marble is due to the presence of impurities. Calcium carbonate occurs naturally in amorphous masses and in crystals of different forms. When precipitated from solutions of calcium salts by soluble carbonates, it comes down at first as amorphous scales and later as minute crystals. It is only very slightly soluble in pure water, but it is more soluble in water containing dissolved carbon dioxide (§ 330).

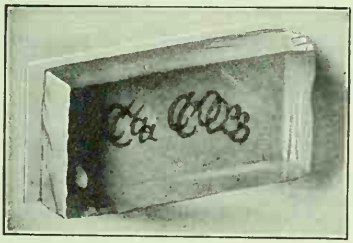


FIGURE 159.

Calcite, a transparent crystalline variety of calcium carbonate. It has the property of double refraction in a marked degree.

378. Hard Waters. — The solubility of calcium carbonate in water containing an excess of carbon dioxide explains the formation of the kind of *hard water* that is found in regions where limestone is abundant. The surface water, becoming charged with carbon dioxide from decay going on in the soil, dissolves some of the limestone, converting it into calcium bicarbonate.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

If an attempt is made to use soap with such water, it is found difficult to obtain a lather, as the calcium ions react with the soap to form an *insoluble* soap. By boiling hard water of this kind, part of the carbon dioxide is driven off and the calcium bicarbonate is converted into calcium carbonate:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

The carbon dioxide escapes and the calcium carbonate is precipitated. The hardness of water in limestone regions causes it to form a firmly adhering deposit on all vessels in which it is boiled, since boiling decomposes the calcium bicarbonate, driving off part of its carbon dioxide and leaving the insoluble carbonate. This deposit, known as *boiler scale*, is a poor heat conductor, and clogs the tubes of steam boilers. Hence the water is often softened before being introduced into the boilers. If the rocks contain magnesium carbonate, this may be converted into the bicarbonate and dissolved in the same way as with the calcium compound, and the water may be softened by the same means. Water containing such dissolved bicarbonates is called "*temporary*" hard water. "*Permanent*" hard water generally contains *sulphates* of calcium and magnesium and cannot be softened by boiling.

In one process of water softening, slaked lime, $Ca(OH)_2$, is thoroughly mixed with water in the chemical tank (Fig. 160), and then fed into the top of a long, vertical softening tank. Revolving paddles in this tank thoroughly mix the lime with the water to be softened, and the following reaction takes place:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$

As the water passes out of the bottom of the inner compartment and up through the larger tank surrounding it, most of the calcium carbonate and other solid impurities settle out. Any remaining solids are removed by the filter, and the softened water flows from the outlet at the top. If the water contains permanent hardness, sodium carbonate is used with the lime.

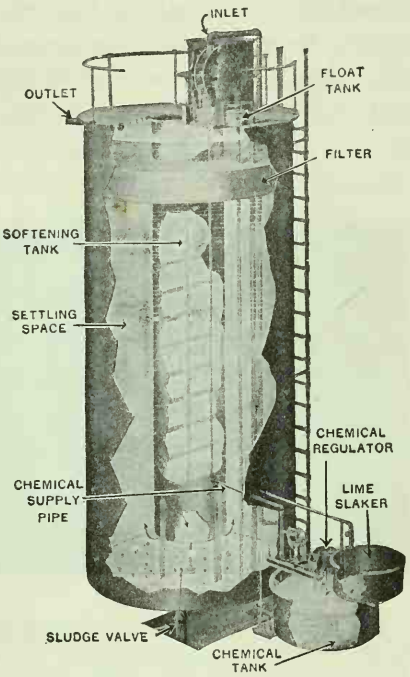


FIGURE 160.

A tank which uses, on a large scale, the fact that calcium bicarbonate can be precipitated as insoluble calcium carbonate by the addition of slaked lime. The mixing is done in the central tank that is provided with paddle-wheels. Settling occurs in the larger tank, and filtering is accomplished at the top.

379. Limestone Caves. — The formation of underground caverns in limestone regions is due to the dissolving action of carbonic acid on calcium carbonate. Charged with carbon dioxide from decaying organic materials, the soil water dissolves the limestone and sinks through cracks in the rock, widening them as it goes. Reaching a less soluble stratum of rock, it flows along this, but dissolves the limestone above. This action, continuing for centuries, finally excavates a cave, such as Mammoth Cave in Kentucky and Luray Cavern in Virginia. As soon as these caves are hollowed out, a new process sets in. The water, before it drops from the roof, loses some of its carbon dioxide, and part of the bicarbonate is converted into the insoluble carbonate. This is left behind on the roof of the cave. The drops that fall to the floor lose more carbon dioxide and some water by evaporation, and likewise deposit calcium carbonate. The final result of the process is the formation of hanging masses of calcium carbonate, like icicles of stone, known as *stalactites*, and the formation of round mounds below called *stalagmites* (Fig. 161). These in turn finally unite to form columns. In this way the cave may become nearly filled again

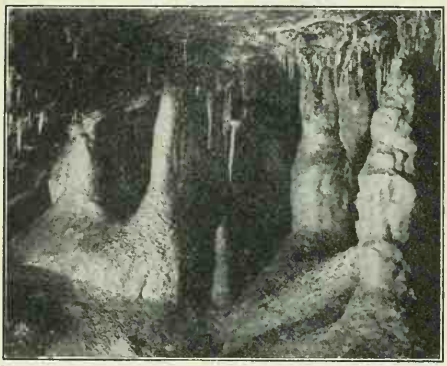


FIGURE 161.

This limestone cave is slowly refilling itself by the formation of stalactites (from the top) and stalagmites (from the bottom).

380. Uses of Calcium Carbonate. — Natural calcium carbonate has three very important uses. Large quantities of limestone and marble are used as *building stone*. Enormous amounts of limestone are yearly "burned" (heated to expel the carbon dioxide) to form *quicklime* and cement. Much limestone is used in the production of cast iron (§ 414). Finely ground limestone is frequently used on farm land, to neutralize undesirable acids that may be present in the soil.

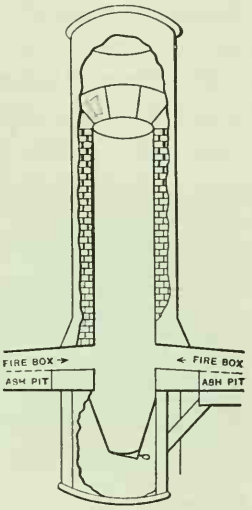


FIGURE 162. — A LONG FLAME LIME KILN.

The fire boxes are arranged on opposite sides near the bottom so that the lime will not be contaminated with ashes. Limestone is put in at the top and the finished lime is taken out at the bottom. The operation is continuous.

CALCIUM OXIDE

381. Manufacture of Lime. — Calcium oxide, or *quicklime*, is made by the decomposition of calcium carbonate at a red heat:

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

The manufacture of lime is carried on in special furnaces called *lime kilns* (Figs. 162, 164). In the modern lime kilns (Fig. 162), the fire is in side chambers and only the hot gases find their way up through the charge of limestone fed in at the top of the furnace. In this *long flame process*, the lime withdrawn at the bottom of the kiln is free from ashes.

If the limestone contains impurities, as silica, iron, or alumina, in any considerable amount, a poor quality of lime is obtained. The operation of the kiln depends upon the

efficient removal of the carbon dioxide, so that it does not cause a reversal of the reaction. Steam or air is blown through the kiln for this purpose. This constitutes a practical application of the law of mass action (§ 172).

382. Rotary Lime Kiln. — The best lime is made in a rotary kiln (Fig. 164), in which limestone, crushed to one-inch pieces, slowly passes down the rotating cylinder and meets an intensely hot flame from the burning of a blast of hot air and producer gas (or pulverized coal). The flame extends a considerable distance into the kiln, and the intense heat completely expels the carbon dioxide from the pieces of limestone as they turn over and over. The hot lime at the lower end of the kiln drops into a rotary cooler. Here it gives up its heat to the air that is used for the kiln blast. Heat economy is secured not only in this way, but also by passing the hot gases from the top of the kiln through the dust settling chamber to the boiler, where these gases generate all the steam necessary for the gas producer and for driving all the machinery connected with the kiln. Few manufacturing processes are operated with so complete a utilization of the heat generated.

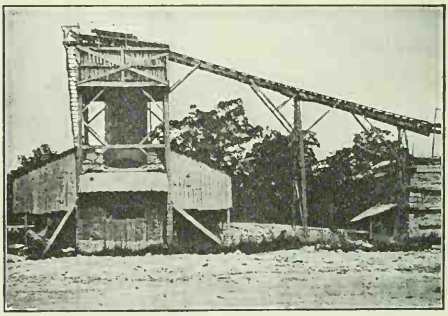


FIGURE 163. — A PHOTOGRAPH OF A LONG FLAME LIME KILN.

The inclined runway affords a means of carrying limestone to the top. The sheds house the fire boxes.

The rotary kiln produces a thoroughly and carefully burned lime, free from dust and ashes. Its small and uniform pieces permit compact packing, and for this reason the lime is less liable to air-slake than the larger lumps of varying size produced by other kilns. Moreover, it slakes with water more rapidly and evenly than lime made by other processes.

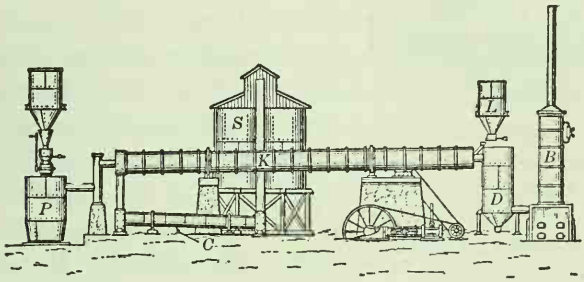


FIGURE 164. — A ROTARY LIME KILN.

Limestone in small lumps passes from *L* into *K*, where uniform heating is assured by the constant rotation of the cylinder. The lime is cooled in *C*. The heat of escaping gases is utilized in *B* to provide steam to run the engine.

383. Properties. — Pure calcium oxide is a white, non-crystalline substance that can be fused and vaporized only at the temperature of the electric arc (about 3500°).

When water is put on lumps of quicklime, cracks soon appear on the surface, the mass swells, and finally falls to a voluminous white powder or a pasty mass, according to the amount of water added. The heat of combination is so great that the lime becomes hot, and clouds of steam arise. This energetic action or process is called *slaking*, and the product of the reaction, calcium hydroxide, is called *slaked lime*.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

When quicklime is left exposed to the air, both water and carbon dioxide are taken up, with the formation of both calcium hydroxide and calcium carbonate. This process is known as *air-slaking*. On continued exposure to the air, the calcium hydroxide slowly changes to calcium carbonate.

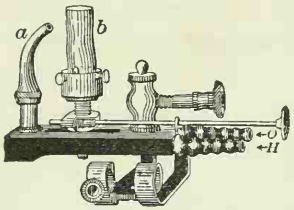


FIGURE 165.

a is an oxyhydrogen blowpipe. It heats the lime cylinder (*b*), and a powerful light of dazzling whiteness is produced.

384. Uses. — On account of its infusibility and its dazzling incandescence when heated in the oxyhydrogen flame, calcium oxide is used in the calcium or lime light. A lime-light burner is shown in Figure 165. Calcium oxide and hydroxide are sometimes used to neutralize acids in soils.

CALCIUM HYDROXIDE

385. Properties and Uses. — Calcium hydroxide, or slaked lime, is a white solid when pure, and is sparingly soluble in water, forming a solution called *limewater*. Limewater, white with suspended but undissolved particles of the hydroxide, is known as *milk of lime*. *Hydrated lime* is calcium hydroxide obtained by the reaction of calcium oxide with just sufficient water to form the hydroxide.

When calcium hydroxide is heated, it loses water and is reconverted into the oxide, showing the reaction to be a reversible one, according to the temperature:

$$Ca(OH)_2 \rightleftarrows CaO + H_2O$$

The water solution of calcium hydroxide is strongly basic, a property which has led to the wide use of the hydroxide

as a cheap alkali. In this respect it stands among the bases as sulphuric acid does among the acids.

Slaked lime, as a cheap base, is used in the manufacture of alkalies and bleaching powder, in glass making, for whitewash, in the removal of hair from hides, and in many other industries. It is employed in *water softening* (§ 378). The chief use of lime, however, is in the preparation of mortar.

386. Mortar. — When sand is thoroughly mixed with wet, freshly slaked lime, ordinary mortar is produced. Mortar is employed to form a hard, stony mass, which holds together the stones or bricks in a building. The hardening of the interior of mortar is due chiefly to the escape of water. The slaked lime at first forms a pasty mass with the water, in which the grains of sand are entangled. This sets to a gel and as the water evaporates, the calcium hydroxide gradually hardens into a compact, stony mass, the sand giving additional strength. At the outer surface of the mortar, which is exposed to the air, the calcium hydroxide reacts with the carbon dioxide of the air, forming calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

This action takes place very, very slowly, and forms a hard protective outer layer. Good mortar increases in strength with age, as the solidity of buildings erected centuries ago shows. Cement (§ 490) is now frequently used in place of part or all of the lime in mortar.

Calcium Sulphate

387. Varieties. — Calcium sulphate is, next to the carbonate, the most abundant and widely distributed salt of

calcium. It occurs as gypsum, $CaSO_4 \cdot 2\,H_2O$. Satinspar, alabaster, and selenite are varieties of gypsum. Selenite is often found in large, transparent crystals, so soft that they can be scratched with the finger nail. Ground gypsum (land plaster) is used for improving soils.

388. Plaster of Paris. — Gypsum is but sparingly soluble in water; its solubility increases to 40° and then decreases. When heated to about 175° C., gypsum loses three quarters of its water of crystallization, and the residue may be said to have one molecule of water of crystallization to every two molecules of calcium sulphate, $(CaSO_4)_2 \cdot H_2O$. The chalky powder resulting from the heating is known as *plaster of Paris*. On a large scale, it is made by heating in huge kettles gypsum, ground to a fine powder and constantly stirred to insure evenness in "burning." Care is taken not to overheat the gypsum.

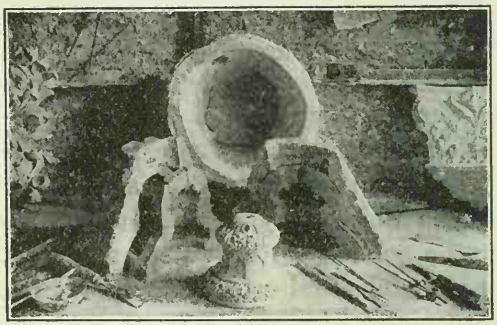


FIGURE 166.
Showing a plaster of Paris cast and the mold from which it was obtained.

389. Plaster Casts. — When water is mixed with plaster of Paris, they unite to form hydrated calcium sulphate,

$$(CaSO_4)_2 \cdot H_2O + 3\,H_2O \longrightarrow 2\,[CaSO_4 \cdot 2\,H_2O]$$

The hardening that accompanies this process is known as "setting." There is a slight increase in volume during the

setting, which explains the use of plaster of Paris in making casts. The slight expansion secures a sharp impression of the mold. The powder is mixed with about a third its weight of water, the pasty mass put into the mold, and in less than half an hour the plaster sets (Figs. 166, 167). The ivory surface of casts is secured by dipping them in melted paraffin or by painting them with a solution of paraffin in petroleum ether. The solvent in the latter case evaporates, leaving the wax in the pores of the cast and making it impervious to water. Plaster of Paris is also used for rigid bandages in surgery and as a surface coating for walls.

FIGURE 167.

Below is the mold from which the plaster cast (above) has been prepared.

390. Calcium Phosphates. — The phosphates of calcium are of great importance to organic life. The mineral matter in bones of animals is essentially *normal calcium phosphate*, $Ca_3(PO_4)_2$. This compound occurs as phosphorite, which has been derived from animal remains. *Guano* contains phosphates in addition to nitrogenous compounds. Phosphates are an important plant food, but to be available must be in a soluble form that can be taken up by the plants. The phosphates that occur in the soil are very insoluble, and since their natural conversion into soluble phosphates is very slow, the supply of soluble phosphates in cultivated soils often becomes scanty. To supply this need, the manufacture of

soluble phosphates for fertilizers has grown to be an important industry.

The monocalcium phosphate, or *superphosphate of lime*, $Ca(H_2PO_4)_2 \cdot 2\ H_2O$, is a very important artificial fertilizer. It is made by treating rock phosphates with crude sulphuric acid. The superphosphate formed is soluble in water, so that it is available for plant use when spread upon the soil. Pure monocalcium phosphate is used in baking powders.

391. Bleaching Powder. — Bleaching powder, or chloride of lime, is made by passing chlorine over freshly slaked lime on the floors of a series of absorption chambers (Fig. 168).

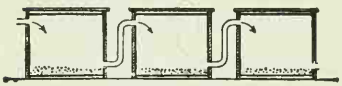


FIGURE 168.

In making bleaching powder, chlorine passes through a succession of chambers on whose floors calcium hydroxide has been spread.

Bleaching powder is an unstable white powder which is slightly soluble in water. Its composition corresponds to the formula $CaCl \cdot ClO$, or $CaCl_2O$. When bleaching powder is treated with an acid, in bleaching, chlorine is first liberated and then this combines with water, forming hypochlorous acid, which removes the coloring matter (§ 94):

$$CaCl_2O + 2\ HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$
$$Cl_2 + H_2O \longrightarrow HClO + HCl$$

The cotton to be bleached is freed from grease and oil. It is next soaked in a solution of bleaching powder, then dipped in dilute acid, next in a solution of "anti-chlor," and finally thoroughly washed to remove the chemicals (cf. § 94). The solutions used are very weak, to prevent injury to the fiber of the cloth.

When exposed to the air, bleaching powder slowly reacts

with the carbonic acid formed by the union of carbon dioxide with water. As a result chlorine is liberated, and hence bleaching powder is used as a disinfectant and germicide.

SUMMARY

Calcium, although very abundant in nature, is rarely seen as metal. It can be obtained by the electrolysis of fused calcium chloride.

The most important **calcium compounds** are:

the carbonate (limestone, chalk, marble);
the hydroxide (slaked lime);
the oxide (quicklime);
the phosphate (phosphorite);
the sulphate (gypsum).

Lime is made by heating calcium carbonate. **Slaked lime** is made by adding water to quicklime. **Air-slaked lime** is a mixture of calcium hydroxide and calcium carbonate, formed by the exposure of quicklime to air.

Slaked lime is used in making mortar, which hardens by the evaporation of water and the absorption of carbon dioxide.

Plaster of Paris is made by partly dehydrating gypsum. It is used in making plaster casts.

Calcium phosphates are contained in bones and in rock deposits. The insoluble phosphates in rock deposits are made soluble for use in manufacturing fertilizers by treating them with sulphuric acid.

Bleaching powder is made by passing chlorine over slaked lime. It is used in bleaching and as a disinfectant.

EXERCISES

1. Write the equations for the reaction between water and (*a*) sodium, (*b*) calcium. How do the reactions differ in intensity?

2. What is the deposit in tea kettles in which hard water has been boiled?

3. Explain the formation of stalactites and stalagmites.

4. How much quicklime can be obtained from four tons of limestone containing 98% of calcium carbonate?

5. Why is the production of lime hastened by blowing air or steam into a lime kiln?

6. In the laboratory, loosely stoppered bottles that contain quicklime are sometimes found with the sides broken out. How do you account for this?

7. Write the equations that illustrate the formation of air-slaked lime.

8. What weight of water enters into combination in slaking 500 pounds of quicklime, 95% pure?

9. Lime water standing exposed to air becomes coated with a film of insoluble substance. What is the substance? Explain its formation.

10. How could quicklime be made from slaked lime?

11. What weight of nitric acid would be required to neutralize 35 grams of calcium hydroxide?

12. Compare the hardening of mortar with that of plaster of Paris.

13. For what reason is normal calcium phosphate converted into " superphosphate " in the manufacture of fertilizers?

14. Why is bleaching powder shipped in air-tight containers?

15. Account for the disinfecting power of " chloride of lime."

16. Calculate the weight of quicklime that one might expect to get from 1000 kilograms of pure limestone. What weight of carbon dioxide would be given off during the action? What volume would the gas have, standard conditions?

CHAPTER XXIX

MAGNESIUM, ZINC, AND MERCURY

Magnesium

392. Occurrence and Preparation. — Although magnesium is of comparatively little commercial importance, its compounds are very abundant in nature. The most important of these are *dolomite*, a double carbonate of calcium and magnesium, $CaCO_3 \cdot MgCO_3$; *magnesite*, $MgCO_3$; *carnallite*, a double chloride of potassium and magnesium, $KCl \cdot MgCl_2 \cdot 6\ H_2O$; *kainite*, a double salt of potassium chloride and magnesium sulphate, $KCl \cdot MgSO_4 \cdot 3\ H_2O$. Magnesium is also found in combination with other elements in various natural silicates, for example, hornblende and asbestos. *Epsom salts*, magnesium sulphate, $MgSO_4 \cdot 7\ H_2O$, is found in some springs whose waters owe their laxative properties to its presence.

The metal is commercially obtained by the electrolysis of the chloride. The salt is fused, together with some common salt or with cryolite, in an iron crucible which acts as the cathode. A carbon rod serves as the anode.

393. Properties and Uses. — Magnesium is a silvery white metal of low specific gravity. It resembles both calcium and zinc in its properties, and stands between them in metallic character. It decomposes water slowly at 100°, but does not affect it at ordinary temperatures. Moist air acts on magnesium slowly, forming a basic carbonate of

magnesium. Magnesium burns with comparative ease, with the evolution of a brilliant white light that has great power to affect the photographic plate. The oxide is formed by this reaction:

$$2\ Mg + O_2 \longrightarrow 2\ MgO$$

Dilute acids react with magnesium very readily, hydrogen usually being evolved.

Magnesium is one of the few elements that enter into direct combination with nitrogen. When nitrogen is passed over red-hot magnesium, magnesium nitride, Mg_3N_2, is formed.

Magnesium is sometimes used in flashlight preparations for photographic purposes because the light that it gives in burning is rich in violet and ultraviolet rays. It is also used in making fireworks, and in many light alloys.

394. Compounds of Magnesium. — The common salts of magnesium are stable substances and, with the exception of the carbonate and the phosphate, are soluble in water. The formulas of the magnesium compounds show that the element has a valence of two, that is, it forms Mg^{++} ions.

Mixtures of magnesium carbonate with magnesium hydroxide are used in pharmaceutical preparations and in face powders. Talc, used for making talcum powder, is natural magnesium silicate.

Magnesium citrate and sulphate are valued on account of their medicinal properties. The sulphate is the medicinal constituent of many commercial laxative waters. Magnesium chloride is used to some extent in preparing fireproofing materials and in the manufacture of disinfectants.

Many magnesium compounds, when heated in an oxidizing flame, are converted into magnesium oxide. This, when

moistened with a solution of cobalt nitrate and heated, yields a mass having a pale pink color.

Zinc

395. Minerals are the elements and compounds whose mixtures make up the inorganic material of the earth. Copper, sulphur, rock salt (NaCl), silica (SiO_2), calcite ($CaCO_3$), and hematite (Fe_2O_3) are examples of minerals.

Ores are the natural deposits from which elements, especially the metals, are extracted. An ore is seldom composed of one mineral.

396. Extraction of Zinc from Its Ores. — Zinc is not found in the uncombined state. Some of its common ores are zinc blende, ZnS; smithsonite, $ZnCO_3$; zincite, ZnO.

To separate zinc from the oxide, the ore is finely powdered and mixed with coal dust. The mixture is then heated in earthenware retorts (Fig. 169, *a*). The carbon reduces the zinc oxide, as shown by the equation:

$$ZnO + C \longrightarrow Zn + CO\uparrow$$

The temperature in the process is raised above 925°, the boiling point of zinc, which therefore passes off as a gas, and is condensed in earthenware or iron receivers (*b*).

When the ore is not an oxide, a preliminary operation must precede the reduction. This consists in heating the ore on grates in contact with air. The operation is known as *roasting*, and converts the metal into an oxide. In the case of zinc sulphide, care is taken not to convert it into the sulphate.

$$ZnCO_3 \longrightarrow ZnO + CO_2\uparrow$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2\uparrow$$

The oxide that results in these reactions is then reduced with carbon in the manner that has been described.

Zinc, as extracted from its ores, usually contains carbon, arsenic, cadmium, and other impurities. It is freed from these by distillation.

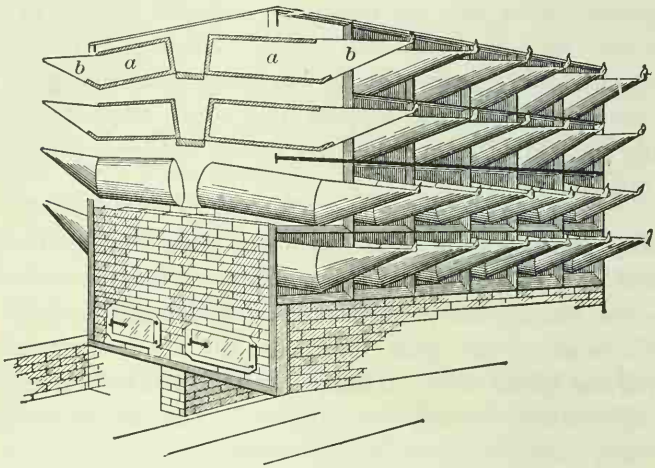


FIGURE 169.

A bank of twenty-four retorts where zinc oxide is being reduced by carbon. The metal distils into the conical receivers which cap the ends of the retorts. The carbon monoxide formed burns at the tips of the receivers.

397. Physical Properties. — Zinc is bluish white in color. It comes into the market in the form of heavy bars, called *ingots* or *spelter*, formed by pouring the melted metal into molds. In this form, the metal is crystalline in structure and rather brittle. Between 100° and 150° C. it is malleable and ductile, and can be rolled into sheets. After having been obtained in this form, it remains malleable at ordinary temperatures. At 300° it again becomes brittle and can be powdered.

Granulated zinc is a form much used in the laboratory. It is made by pouring the melted metal drop by drop into water. *Zinc dust* is obtained by the sublimation of the metal. As long as the receiver remains comparatively cold, the distilled zinc collects in the form of a powder. This operation is similar to the one by which sulphur is obtained as flowers of sulphur. Zinc dust always contains a certain amount of the oxide.

398. Chemical Properties. — Zinc is regarded as distinctly metallic, but it differs considerably from such metals as calcium and sodium. It resembles magnesium more closely. Zinc does not act on water at ordinary temperatures. Air attacks it slowly in the presence of moisture, forming a basic carbonate, which acts as a protective coating, so that only the outer layer of the metal is affected. When zinc is heated in air or oxygen, it burns with a bluish flame, forming zinc oxide:

$$2\,Zn + O_2 \longrightarrow 2\,ZnO$$

Zinc reacts readily with dilute acids, forming zinc salts, and, as a rule, liberates hydrogen:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2\uparrow$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

In acting on zinc (or other metals), nitric acid and concentrated sulphuric acid do not liberate hydrogen, since they act as oxidizing agents and convert the hydrogen into water. In these cases, the gas that is given off is a reduction product of the acid used.

The action of dilute acids on zinc is hastened by the presence of certain solid substances in contact with the metal. Pure zinc will scarcely react with acids, but commer-

cial zinc, which may contain carbon, dissolves with great rapidity. A similar effect is produced by the presence of a very small amount of copper, or other metal, in contact with the zinc. In these cases, the particles of carbon or copper act like cathode plates of a voltaic cell; hence the velocity of the evolution of hydrogen from acids is increased by their presence.

Zinc reacts with solutions of potassium hydroxide to form potassium zincate and hydrogen:

$$Zn + 2\ KOH \longrightarrow K_2ZnO_2 + H_2 \uparrow$$

When hydrochloric acid is added to potassium zincate, zinc hydroxide is first formed and then reacts with an excess of hydrochloric acid to form zinc chloride.

$$K_2ZnO_2 + 2\ HCl \longrightarrow Zn(OH)_2 + 2\ KCl$$
$$Zn(OH)_2 + 2\ HCl \longrightarrow ZnCl_2 + 2\ H_2O$$

Many compounds of zinc, when heated on charcoal or on a plaster of Paris block in a blowpipe flame, yield zinc oxide, yellow when hot, and white when cold. If the oxide is moistened with a drop of a solution of cobalt nitrate, and again heated, a bright green mass containing a compound of zinc and cobalt oxides is obtained. This affords a convenient test for a zinc compound.

399. Uses. — Zinc is used in making several important *alloys*, or solid solutions of two or more metals. *Brass* (Fig. 170) is composed of copper and zinc; *German silver* contains copper, zinc, and nickel; *bronze* sometimes contains zinc in addition to copper and tin. Another use of zinc is for the active plates of electric cells. The cylindrical container of a dry cell is zinc and serves as the negative plate.

Galvanized iron is iron covered with a thin layer of zinc, which acts as a protective coating and prevents rusting. The older process for galvanizing consists of thoroughly cleaning the iron by immersing it in an acid solution to remove rust (pickling), treating it with some other cleaning solution, and then dipping it into molten zinc. The zinc forms an alloy with the surface of the iron. A more recent process for galvanizing consists in plating the iron with zinc. The electrolytic bath generally consists of a solution of either zinc sulphate, or zinc sulphate mixed with other salts.

Courtesy of the Cleveland Dental Mfg. Co.

FIGURE 170.

This piece of brass has been etched by dilute acid and a photograph taken through a microscope. It is an example of metals in solid solution.

400. Zinc Oxide and Hydroxide. — Zinc oxide, ZnO, is much used as a white pigment for paints. It does not have as great covering power as white lead, but it has the advantage of not turning black from contact with hydrogen sulphide. It can be made by burning zinc or by heating zinc hydroxide or zinc carbonate:

$$Zn(OH)_2 \text{ (heated)} \longrightarrow ZnO + H_2O\uparrow$$

$$ZnCO_3 \quad \text{(heated)} \longrightarrow ZnO + CO_2\uparrow$$

A mixture of zinc oxide and white lead is considered preferable to either alone, as zinc oxide scales, while white lead powders or chalks on being exposed to the weather. In paints containing a mixture of zinc oxide and white lead, these two

tendencies counteract each other to some extent and the paint is made more durable. Zinc oxide is also used in the preparation of rubber for tires.

On adding potassium hydroxide to a solution of a zinc salt, zinc hydroxide is precipitated, since this substance is insoluble in water. If an excess of potassium hydroxide is added, the hydroxide is dissolved, forming potassium zincate:

$$ZnCl_2 + 2\ KOH \longrightarrow 2\ KCl + Zn(OH)_2 \downarrow$$
$$Zn(OH)_2 + 2\ KOH \longrightarrow K_2ZnO_2 + 2\ H_2O$$

The last equation illustrates the capability shown by several metals, such as zinc and aluminum, of acting as non-metals when in the presence of strong bases.

401. Salts of Zinc. — *Zinc chloride*, $ZnCl_2$, is obtained by the action of hydrochloric acid and zinc. It is an extremely deliquescent substance, sometimes used as a drying agent. It also has the power to dissolve metallic oxides; because of this property its solutions make good soldering fluids for metals. Wood that has been soaked in a solution of zinc chloride resists decay. Zinc chloride is also used as a solvent for cellulose.

Zinc sulphate, $ZnSO_4$, is used in making battery solutions.

402. Zinc sulphide, ZnS, found in nature as zinc blende, can be prepared by the direct combination of zinc dust and sulphur, or it can be precipitated from solutions of zinc salts by the addition of hydrogen sulphide, but the separation of zinc sulphide is not complete:

$$ZnCl_2 + H_2S \rightleftarrows ZnS \downarrow + 2\ HCl$$

The reason that this reaction does not go to completion lies in the fact that zinc sulphide is soluble in a solution that contains a small concentration of H^+ ions. A knowledge of the law of mass action enables us to control the action and make it go to completion in either direction.

Hydrogen sulphide ionizes to only a small degree:

$$H_2S \rightleftarrows 2\,H^+ + S^{--}$$

If we add to the same solution hydrochloric acid:

$$HCl \rightleftarrows H^+ + Cl^-$$

we increase the concentration of the H^+ ions very decidedly. Because of the increase in the hydrogen ions, the precipitation of zinc sulphide is completely prevented in a solution to which hydrochloric or other strong acid has been added.

On the other hand, if we add to the solution a base, such as ammonium hydroxide:

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

the OH^- ions thus produced combine with the H^+ ions of the hydrogen sulphide to form undissociated water and the H^+ ions are thereby removed from the solution. Hence in the presence of a strong base there is little tendency to reverse the action of hydrogen sulphide on the zinc chloride and the precipitation of zinc sulphide is practically complete. Therefore zinc sulphide is not precipitated by addition of hydrogen sulphide to solutions of zinc salts in the presence of a strong acid; zinc is completely precipitated as the sulphide in the presence of a strong base. This fact is made use of in separating and identifying zinc in analytical operations.

All soluble zinc salts are poisonous.

Mercury

403. Occurrence and Separation. — Mercury is found only in a few localities of which the deposits of the United States are now the most important. The chief ore of mercury is *cinnabar*, HgS. Mercury is obtained from cinnabar by heating in contact with air (roasting) in order to convert the sulphur into sulphur dioxide and to vaporize the mercury:

$$HgS + O_2 \longrightarrow Hg\uparrow + SO_2\uparrow$$

The crude mercury vapor thus obtained is condensed and purified.

404. Physical Properties. — At ordinary temperatures, mercury, commonly known as *quicksilver*, is a silvery-white liquid metal, with a brilliant luster. Its density is greater than that of lead, so that iron easily floats on it. Mercury solidifies to a substance resembling tin at about $-40°$ C, and boils at a temperature below red heat, but vaporizes slowly at ordinary temperatures. It is a good conductor of electricity. The molecular weight of mercury, as found from its vapor density, is the same as the atomic weight, 200; hence there is one atom in the molecule of mercury vapor.

The vapor of mercury is highly poisonous, as is the metal itself when finely divided.

405. Amalgams are alloys containing mercury. Mercury dropped on a gold ring will whiten it by amalgamating with the gold. These amalgams are not true compounds, as they have a varying composition. When there is a large excess of mercury, amalgams are liquid; otherwise they are solid.

406. Chemical Properties. — Mercury combines readily with the halogens and with sulphur. Oxygen does not combine with it at ordinary temperatures, but at high temperatures it forms oxides, which at still higher temperatures dissociate into mercury and oxygen. This is shown by the reversible equation:

$$2\,Hg + O_2 \rightleftarrows 2\,HgO$$

Pure dilute acids do not attack mercury. Concentrated nitric acid dissolves it readily, and dilute nitric acid also attacks it in the presence of nitrogen peroxide. Zinc and copper displace mercury from solutions of its salts and furnish a simple means of testing for a soluble salt of mercury.

$$Cu + Hg^{++} + 2\,NO_3^- \longrightarrow Cu^{++} + Hg + 2\,NO_3^-$$

407. Uses. — The facts that mercury is the heaviest liquid and that it is not readily acted upon by atmospheric agents, make mercury very useful in important scientific instruments, such as thermometers and barometers. Pure mercury does not wet glass, and this fact furnishes a very sensitive test for the purity of the metal. It is also used for the collection of gases that are soluble in water. Its most important uses, however, are in the various amalgams. Amalgams of silver and other metals are used in filling teeth. Mercury can be obtained as a fine gray powder by shaking it violently with flour, grease, or any substance that will coat the minute drops and prevent them from uniting to form a fluid. This process, known as *extinguishing*, is used in the preparation of blue pills and mercurial ointments.

Other uses of mercury and its compounds are in the manufacture of fulminates for explosive caps, in electrical appliances, and in the preparation of paints.

Compounds of Mercury

Mercury forms two series of compounds, the mercurous (Hg^{+}) and the mercuric (Hg^{++}). The chlorides are the most important salts, and may be taken as typical of the two series.

408. Mercurous Chloride, HgCl. — Since it is insoluble in water, it may be prepared by treating a solution of a mercurous compound with a soluble chloride. It is produced commercially by heating a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg \longrightarrow 2\,HgCl$$

Mercurous chloride is a white powder, extensively used in medicine under the name of *calomel.*

409. Mercuric Chloride, $HgCl_2$. — The common names of mercuric chloride are *corrosive sublimate* and *bichloride of mercury.* Mercuric chloride is made by heating a mixture of sodium chloride and mercuric sulphate; the chloride sublimes, as its name indicates. The sublimate is a white, translucent mass, from which the salt can be obtained in silky needles by dissolving in water and recrystallizing. It is slightly soluble in water at ordinary temperatures, but is quite readily soluble in hot water. *Corrosive sublimate is a violent poison, and should never be kept with other medicines.* It is also a powerful antiseptic and germicide. For this purpose, very dilute solutions are used (1 part to 2000 to 5000 parts of water). With the alkaline chlorides it forms double salts more soluble than mercuric chloride by itself, and much used in making antiseptic solutions.

410. Other Compounds. — The nitrates of mercury are the soluble mercury compounds most frequently met in

the laboratory. Mercuric oxide is used in the preparation of paints for ship bottoms. These paints are sufficiently poisonous to prevent the fouling of the bottom by marine growths. The paint pigment known as *vermilion* is mercuric sulphide.

SUMMARY

Magnesium

Atomic weight 24. Valence 2.

Magnesium is of little commercial importance. It is used in making several light alloys, in fireworks, and in flashlight powders.

Magnesium is one of the few metals that combine directly with nitrogen.

Common magnesium salts, with the exceptions of the carbonate and phosphate, are soluble in water.

Several magnesium salts are used in **medicine**.

The **carbonate** and the **hydroxide** are used in face powders and in the manufacture of other pharmaceutical preparations.

Epsom salts is crystallized magnesium sulphate, $MgSO_4 \cdot 7\ H_2O$.

EXERCISES

1. For what is magnesium used?

2. Magnesium oxide is slightly soluble in water. Would the solution give an alkaline or an acid reaction? Why?

3. What reaction takes place when dilute sulphuric acid is added to magnesium?

4. Mention two ways by which carbon dioxide could be obtained from magnesite.

5. What is Epsom salts?

6. How many grams of magnesia, MgO, could be prepared by heating 20 grams of magnesium carbonate? How many liters of carbon dioxide would be liberated?

7. When 0.362 gram of magnesium was added to an excess of dilute hydrochloric acid, 365 c.c. of hydrogen was liberated. At the time the measurement was made, the temperature was 21° C. and the pressure was 770 mm. From the data given calculate the hydrogen equivalent of magnesium.

SUMMARY

Zinc

Atomic weight 65. Valence 2. Melting point 419°. Boiling point 925°.

A mineral is an inorganic element or compound occurring naturally in the earth.

An ore is a natural deposit from which some useful element, generally a metal, can be extracted.

Zinc is usually **obtained** by roasting the ore, to produce zinc oxide, and then reducing the oxide.

Spelter, sheet zinc, granulated zinc, and zinc dust are **commercial forms** of zinc.

Brass and German silver are common **alloys** of zinc.

Zinc is an **amphoteric element**, since it acts like a metal with acids and like a non-metal with strong bases.

Zinc hydroxide acts as a base in the presence of strong acids and as an acid in the presence of strong bases.

Zinc oxide is used in the preparation of zinc ointment; it is also used in making white paint and in vulcanizing rubber.

Zinc chloride is used to clean metals preparatory to soldering; as a wood preservative; as a solvent for cellulose.

Zinc sulphide is white.

Zinc sulphate is used in the preparation of battery fluids and in the manufacture of fireproof paints.

EXERCISES

1. Starting with zinc carbonate, describe the preparation of four commerical forms of zinc.

2. Name two alloys of zinc and tell what each contains.

3. What is galvanized iron?

4. Why does zinc corrode very slowly in air?

5. What advantage is there in using zinc oxide (zinc white) in place of white lead for a paint pigment?

6. Write equations showing how hydrogen could be produced by the reaction of either an acid or a base with zinc.

7. Why is wood sometimes impregnated with a solution of zinc chloride?

8. Why is tin plate, preparatory to soldering, often wet with a solution of zinc chloride?

9. Why will not hydrogen sulphide completely precipitate zinc, as zinc sulphide, from a solution of zinc sulphate?

10. Mention two ways by which zinc sulphide can be formed.

11. Water solutions of zinc sulphate give an acid reaction. Show how hydrolysis explains this fact.

12. Describe a test for zinc.

13. How many grams of zinc would be required to replace the hydrogen contained in 15 grams of sulphuric acid? How many liters of hydrogen would be formed?

SUMMARY

Mercury

Atomic weight 200. Valence 1 or 2. Melting point — 39°. Boiling point 357°. Specific gravity 13.6.

Mercury occurs as the sulphide, from which it is extracted by roasting

Mercury **combines** readily with sulphur and the halogens. At temperatures a little below its boiling point it combines with oxygen. Concentrated nitric acid is the only acid that has much effect on mercury at ordinary temperatures.

It is the only metal that is a **liquid** at ordinary temperatures.

Mercury is **used** in scientific and electrical instruments and in the preparation of pigments and amalgams.

Calomel, mercurous chloride, is used in medicine.

Corrosive sublimate, bichloride of mercury, or mercuric chloride, is a deadly poison and is used as a germicide.

EXERCISES

1. Write the equation for the extraction of mercury from cinnabar.

2. What properties of mercury make it suitable for use in thermometers? In barometers?

3. What is an amalgam?

4. Under what circumstances is it desirable to collect a gas by the displacement of mercury? Why is it more difficult to collect a gas by the displacement of mercury than by the displacement of water?

5. What would be a simple way of testing a solution for the presence of a mercury salt?

6. Why is mercuric oxide used in paints for ship bottoms?

7. Calculate the percentage composition of the two chlorides of mercury. What law is illustrated by the composition of these compounds?

8. Why do surgeons often wash their hands in a solution of mercuric chloride before performing an operation?

9. Why should bichloride of mercury tablets never be kept in a medicine closet?

CHAPTER XXX

IRON AND STEEL

411. Occurrence of Iron. — A consideration of the enormous number of purposes for which iron is used will show how impossible our present civilization would be without this metal.

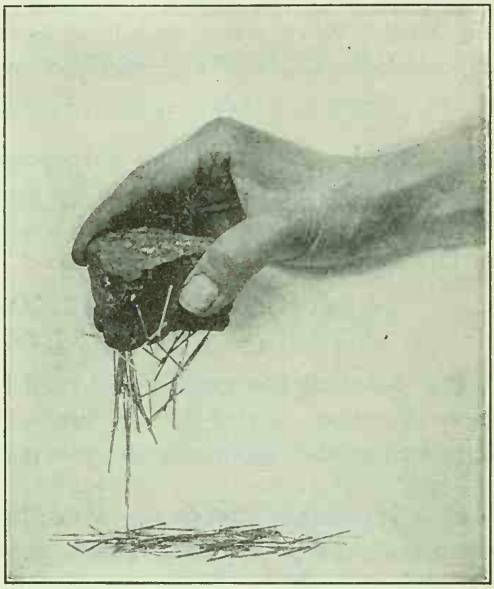


FIGURE 171.

A magnet made by nature. It is composed of magnetic oxide of iron, one of the ores of iron.

Nearly all meteorites contain iron alloyed with nickel. As iron rapidly corrodes when exposed to moist air, native iron is not of common occurrence, but compounds of iron are common. The red and yellow colors of soils are generally due to oxides of iron. The principal ore of iron is hematite mixed with other minerals, such as silica and clay.

412. Formation of Iron Deposits. — When water percolates through a soil containing much vegetable matter, it takes up substances capable of reducing ferric compounds to ferrous compounds. When water containing carbon dioxide comes in contact with the ferrous compounds, ferrous bicarbonate, $Fe(HCO_3)_2$, is formed, which is soluble. In this way, iron is dissolved out of the soil. If the water containing ferrous bicarbonate collects in a warm place *not in contact with air*, carbon dioxide is driven off and ferrous carbonate (siderite), which is insoluble in water, may be deposited. When water containing ferrous bicarbonate is *exposed to the air*, ferric hydroxide is formed:

$$4\ Fe(HCO_3)_2 + 2\ H_2O + O_2 \longrightarrow 4\ Fe(OH)_3\downarrow + 8\ CO_2\uparrow$$

This may be deposited, and, on becoming dry, may lose sufficient oxygen and hydrogen in the form of water to convert it into hydrated ferric oxide (limonite), $2\ Fe_2O_3 \cdot 3\ H_2O$, or into ferric oxide (hematite), Fe_2O_3:

$$4\ Fe(OH)_3 \longrightarrow 2\ Fe_2O_3 \cdot 3\ H_2O + 3\ H_2O$$
$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$

413. Smelting is a general term used to designate one or more operations carried on in a furnace for the purpose of obtaining an element (nearly always a metal) from an ore.

414. Smelting of Iron Ore. — When impure hematite, for example, is to be smelted, it is necessary to accomplish *two* main operations. These are: (*a*) to reduce the oxide, for which purpose carbon in the form of coke is used; and (*b*) to separate the other minerals that occur in the ore; for this purpose a substance called a *flux* is employed. The flux also aids in the fusion of the ore.

When the ore contains sand (silica, SiO_2), limestone is

used as a flux. On being heated in the furnace, the limestone is decomposed into carbon dioxide and calcium oxide:

$$CaCO_3 \longrightarrow CO_2 + CaO$$

The basic oxide, CaO, combines with the acidic oxide, SiO_2, and forms calcium silicate.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

If the ore contains basic material, silicon dioxide may be used as a flux, and the removal of the impurity be effected in a way analogous to that just described.

415. Manufacture of Cast Iron. — Iron ores are smelted in a *blast furnace* (Fig. 172) which has a steel shell from 75 to 90 feet high, lined with a thick layer of fire brick. Cold water is made to circulate through hollow castings built into the fire brick in the part of the furnace where the most energetic chemical action takes place during the smelting. This is just above the point where pipes called *tuyères* admit powerful blasts of hot, dry air into the furnace. The name "blast furnace" is due to these blasts of air.

A blast furnace, once started, is kept in continuous operation day and night, seven days in the week, until it is necessary to shut down in order to make repairs. The charge of ore, coke, and flux is dropped in at the top of the furnace from time to time. The heated blast of air that enters the furnace through the tuyères comes in contact with the burning coke and forms carbon dioxide, which is immediately reduced to carbon monoxide by the excess of hot carbon. The carbon monoxide and remaining carbon reduce the iron oxide to iron:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$
$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$$

Simultaneously with the reduction of the ferric oxide, some silica is reduced to silicon, and combines with the iron. The iron also absorbs sulphur and phosphorus from the ore and coke; and some carbon enters it from the coke. This impure iron settles to the bottom of the furnace, from which place it is drawn off from time to time through a hole, called a tap hole. The stream of white-hot, molten metal is cast into ingots called *pigs* (Fig. 174). The product is known as *pig iron* or *cast iron*. The limestone flux mentioned above combines with the silica and other acidic substances in the ore, and produces the *slag*. Both slag and the molten cast iron collect in the crucible of the furnace, the slag floating on the heavier iron.

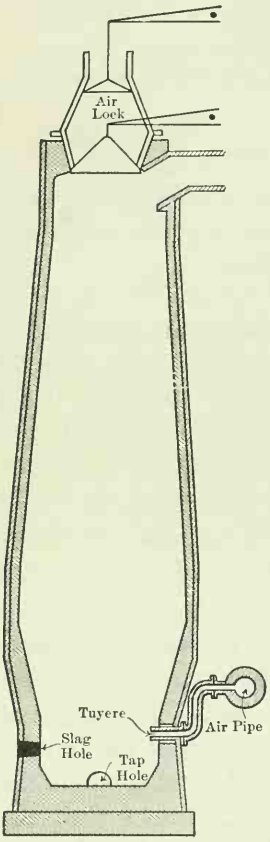


FIGURE 172.

Iron ore, coke, and flux material, with the aid of heat from the burning of part of the coke in blasts of hot air, react to produce cast iron continuously in enormous quantities.

416. The Blast Furnace. — The need of cheap and rapid production of cast iron has brought the blast furnace to its present efficiency. The opening at the top through which the charging is done is closed by a cup-and-cone arrangement (Fig. 172). The best modern furnaces have an air lock at the top, closed above and below by a cup-and-cone. In such a furnace, the

charge can be let into the air lock, and then, after the opening at the top is closed, can be allowed to drop into the furnace. This method prevents the escape of gas during charging. The gases produced during the smelting, which contain about 20% carbon monoxide, are conveyed away from near the top of the furnace through a large flue. This furnace gas is burned to supply heat for the air blast, and under the boilers to generate steam for the engines which compress the air for the tuyères.

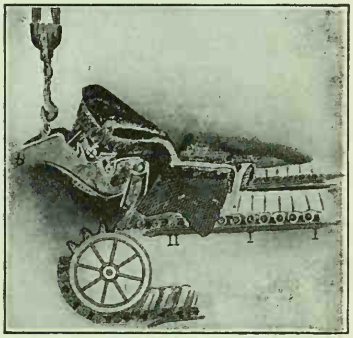


FIGURE 173.

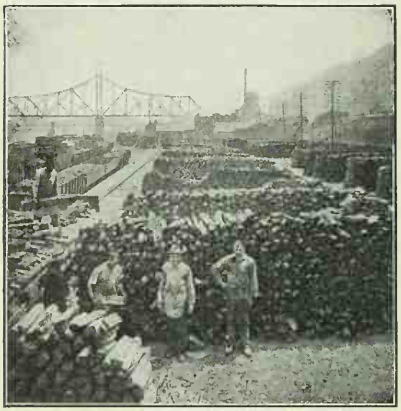
The ladle pours molten cast iron into the molds as fast as they are carried by on the endless chain.

The crucible in which the molten iron and slag collect is about 16 feet in diameter. Holes are drilled through it for the removal of slag and iron. The process is called "tapping" the furnace. As soon as the iron or slag has been removed, the tap hole is closed by a clay plug which is instantly hardened by the heat. The slag is tapped off about every two hours, and the iron every four to six hours. From 80 to 300 tons of metal are drawn off per day. If the iron is to be used in making steel in works near by, it is often carried directly there in large ladles; otherwise it is run into pigs, which may be cast in sand, or, by means of a casting machine, in iron molds (Fig. 173).

417. Composition and Properties of Cast Iron. — If the iron, after being drawn from the blast furnace, is suddenly cooled, a white, crystalline, brittle cast iron is obtained. The

carbon in white cast iron is in chemical combination with the iron as iron carbide, Fe_3C. When the molten iron is cooled slowly, most of the carbon separates in the form of graphite, and a softer product known as gray iron is obtained.

Cast iron contains considerable carbon, always over 2% and seldom above 5%. This large amount of impurity gives cast iron a very low melting point. As iron carbide is a very hard compound, white cast iron is harder than gray.



Copyright by the Keystone View Co.

FIGURE 174.

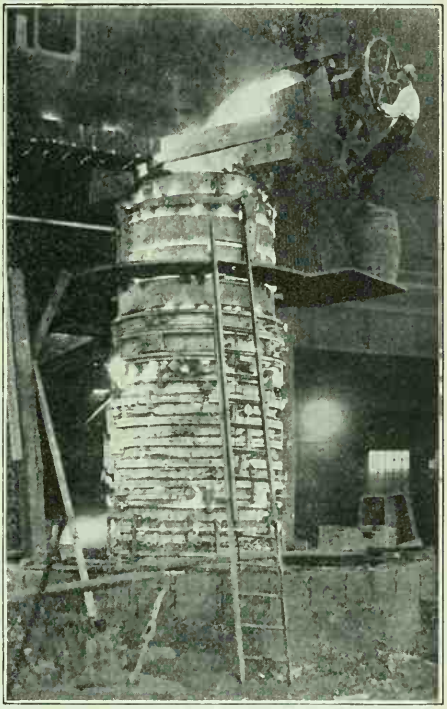
Tons and tons of cast iron in the form of pig iron.

Wrought iron and steel are made from cast iron.

A little iron sulphide is generally formed during the smelting of an iron ore and alloys with the iron. Sulphur makes iron "red short" or, in other words, brittle when red hot. If the ore contains phosphorus, phosphide of iron is formed and dissolves in the iron produced in the blast furnace. Phosphorus makes iron "cold short," that is, brittle when cold.

418. Uses of Cast Iron. — Cast iron is the form of iron most easily melted. When molten cast iron is poured into a mold, and allowed to solidify, the metal readily takes the shape of the mold, because it expands when it passes from a liquid to a solid state. For these two reasons, cast iron is

the cheapest metal to use for making heavy metal objects which are not to be subjected to shock (Fig. 175). In making castings, allowance has to be made for shrinkage, because iron contracts on further cooling after it solidifies. Common cast iron is not malleable and can be neither welded nor tempered. Malleable castings are made by long heating and slow cooling of the cast object.



Courtesy of the Buffalo Foundry and Machine Co.

FIGURE 175.

Cast iron being poured into an enormous mold that has been built up in segments.

419. High-grade Forms of Iron. — Common cast iron is cheap, but its usefulness is limited by the high per cent of carbon and by the sulphur, phosphorus, and silicon that it contains. The problem in making wrought iron and steel consists in controlling the per cent of carbon and in eliminating other impurities.

Removing carbon. — This is accomplished by oxidation. The oxygen used for the purpose comes either from blasts of

air or from iron oxide that is added when the cast iron is put into the furnace. The oxide of carbon escapes along with the other gases that leave the furnace.

Removing phosphorus, sulphur, and silicon. — Oxides of phosphorus and silicon are not volatile at the temperatures that are used in iron furnaces. Their removal and that of the sulphur, which is somewhat more complex, is accomplished by the use of *basic linings.* This invention is due to Thomas and Gilchrist, and the process is named for them. The furnace is lined with a thick coating of calcium oxide or magnesium oxide. The oxides of phosphorus and silicon combine with this basic material to form salts. The lining is renewed periodically, and the old linings are sources of basic phosphates that are valuable as fertilizing material. The material so taken from iron furnaces is sometimes known as Thomas slag.

420. Manufacture of Wrought Iron. — Wrought iron is made in a reverberatory furnace (Fig. 176) by heating cast iron on a layer of iron oxide. The flames of the burning fuel pass over the furnace charge and the heat is reflected downward by the roof of the furnace. The charge is thus melted without coming in contact with the fuel. Under these circumstances, the greater part of the carbon contained in the cast iron is oxidized to carbon monoxide and passes off. The lining, being ferric oxide, is basic and is used to remove sulphur, phosphorus,

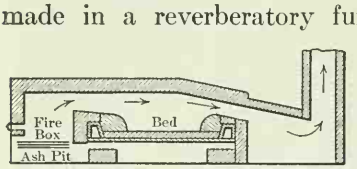


FIGURE 176. — A REVERBERATORY FURNACE.

Flames do not touch the melted metal, and hence carbon is not absorbed from the fuel. The heat of the flames is reflected down from the heavy brick roof.

and silica from the iron. The basic oxides of the ore and furnace lining fuse with the acidic oxides of the impurities to form salts which make up the slag. The iron becomes pasty, because pure iron has a higher melting point than impure. The molten mass in the furnace is stirred or *puddled* and the pasty iron is gathered into large balls called *blooms*. These are removed from the furnace and nearly freed from slag by a process of squeezing and working under a trip hammer. The iron is then rolled so as to give the product a fibrous structure, by causing the remaining slag to be distributed through the iron in the form of fine threads. This small portion of slag aids in the process of *welding* iron.

421. Properties and Uses of Wrought Iron. — Wrought iron is the purest form of commercial iron. Good varieties contain not more than 0.3% of carbon.

When wrought iron is heated, it becomes plastic before melting. When in this condition, two pieces on being hammered together adhere firmly, provided some substance, such as sand, or borax, is placed on the iron to dissolve the thin coating of iron oxide that forms on the heated surface. This process is called *welding*. Plastic wrought iron can be hammered into various shapes, rolled into bars, and drawn into wire. As wrought iron can be readily forged and welded, it is the iron used by the blacksmith. Wrought iron is tough and can be bent or stretched without breaking. It cannot be tempered. It can very easily be converted into a temporary magnet and is therefore used for electromagnet cores. Wrought iron is used to make anchors, chains, wire, and other articles that are intended to withstand sudden and severe strains.

422. Bessemer Steel. — Much cast iron is converted into Bessemer steel, or more properly Bessemer iron. About fifteen tons of molten cast iron are poured into a Bessemer converter (Figs. 177, 178), which is an egg-shaped furnace built of wrought iron plates and lined with a thick layer of refractory material. The bottom is perforated with holes so that streams of air can be blown through the molten metal. The blast lasts from eight to ten minutes, during which time the oxygen of the air unites with the silicon, carbon, and other impurities in the iron, leaving nearly pure iron. The heat of combustion raises the temperature of the metal to a high degree, producing what is known as the "boil." When the blast of air has burned out the impurities, the color of the flame that issues from the mouth of the converter changes and the air is shut off. Since, however, a certain amount of carbon is needed in the finished product, a calculated amount of *spiegeleisen*, which is rich in carbon and manganese, is added. The blast of air is forced through the mass for a short time to mix the ingredients thoroughly. The spiegeleisen furnishes the desired amount of carbon, and the manganese unites with any dissolved oxygen present. The oxygen is thus prevented from

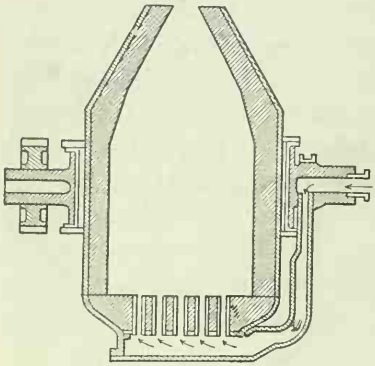
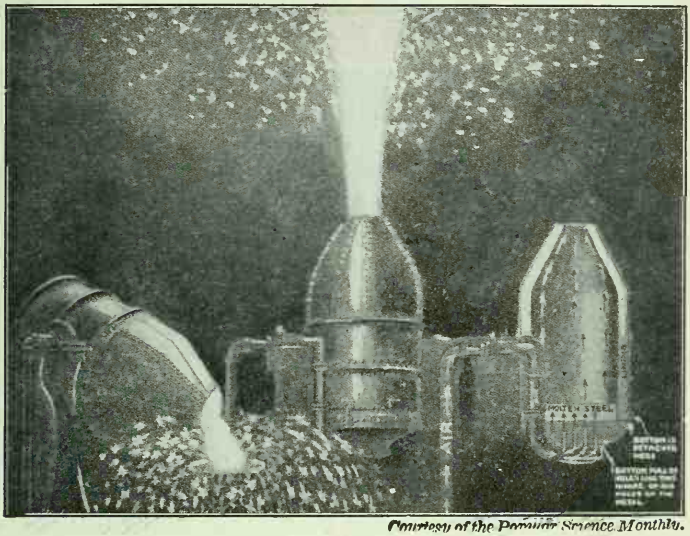


FIGURE 177.

The inventing and perfecting of this Bessemer converter made steel cheap enough for use as the skeletons of great buildings. Air burns out of the cast iron the carbon and the silicon impurities.

escaping and producing blow-holes when the mass cools. The manganese also improves the quality of the metal. At the end of the process, the converter is turned and the contents poured into a ladle and cast.



Courtesy of the Popular Science Monthly.

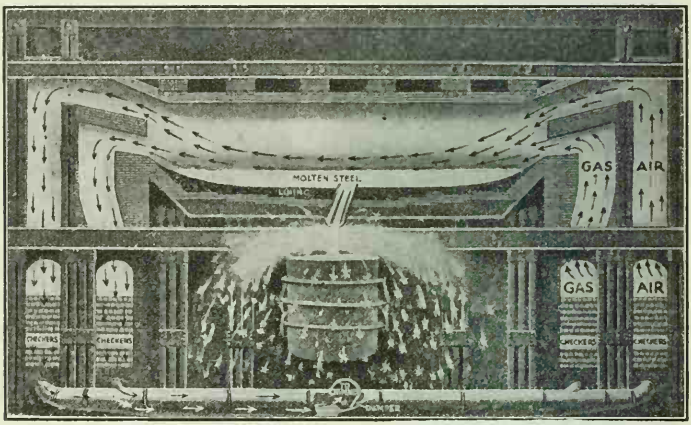
FIGURE 178.

Three views of a Bessemer converter. On the right, a section; in the middle, the furnace is in operation; on the left, the finished product is being poured into molds.

If the pig iron contains sufficient sulphur and phosphorus to injure materially the quality of the Bessemer iron, the converter is lined with basic material.

423. Steel by Open Hearth Process. — Much steel is now made by the open hearth process. An open hearth furnace (Fig. 179) has a large bed lined with fire brick and sand on which the charge is placed. By the aid of a *regen-*

erative heating system, a higher temperature is obtained than would otherwise result. This device is used in many modern furnaces. Gas is used as fuel and is heated before entering the furnace by passing through a checkerwork of hot fire brick. The heated gas is passed into the furnace through a flue, while air that has been similarly heated



Courtesy of the Popular Science Monthly.

FIGURE 179. — AN OPEN HEARTH STEEL FURNACE.

Producer gas and air enter at alternating intervals from either side. The not products of combustion pass out on the opposite side. Thus the gases are pre-heated by passing through brick checkerwork (as in the glass furnace) before passing over the molten steel. A lining serves to remove impurities.

enters through another flue. The burning gas passes over the charge on the furnace bed and the hot, gaseous product escapes through checkerworks which are a duplicate of those used to heat the gas and air. One set of checkerwork is thus raised to a high temperature by the hot combustion products, while the other is being cooled as it heats the gas and air about to enter the furnace. About

every twenty minutes the direction of the gas and air is reversed by means of a system of valves, so that gas and air pass through the recently heated checkerwork while the flame from the furnace passes through the one just cooled.

The furnace charge consists of scrap steel, pig iron, and iron ore. The scrap steel is placed on the bottom in order to protect it from the oxidizing action of the flame. The manganese and silicon are oxidized by the flame, while the iron ore is active in furnishing oxygen to consume the carbon. The process consumes from eight to twelve hours and is watched and controlled most carefully by the operator. Samples of metal are repeatedly taken from the furnace and examined to determine when the impurities have been removed and the carbon has been reduced to the desired amount. In case the pig iron contains phosphorus, a basic furnace lining can be used as in the Bessemer process. The steel produced is of much better quality than the metal made by the Bessemer process and is suitable for the manufacture of connecting rods, shafts, armor plate, heavy ordnance, etc., where great strength and ability to stand vibration are required. It can be forged and tempered. The percentage of carbon varies from 0.2% in soft steel to 2.0%, the maximum in hard steel.

424. Crucible steel is made in graphite crucibles. The materials used are high-grade wrought iron, scrap steel, and carbon, in the form of hard wood charcoal, coke, or graphite. When pure iron is heated to a temperature above 850°, it is converted into an allotropic form of iron that is capable of absorbing carbon. The carbon at first forms a solid solution with the iron, but after the carbon has reached 0.8% of the mass, it separates as iron carbide, Fe_3C. Steel

always contains iron carbide, which may be either dissolved in the iron, or gathered in particles throughout the mass. In general, the more iron carbide the steel contains the harder it is. In the manufacture of crucible steel (Fig. 180), the iron is melted, a temperature of 1500° C. being maintained for from two to six hours. The heating is continued until sufficient carbon has been absorbed from the charcoal

Courtesy of the Crucible Steel Company of America.

FIGURE 180.

High carbon steel for tools is produced in small graphite crucibles. The workman (his feet protected by windings of heavy cloth) is lowering a crucible into the highly heated furnace below.

and the crucible to make the desired quality of steel. Special crucible steels are made by the addition of various substances to the crucible charge. Crucible steels are of high grade and are used in making fine edged tools, springs, automobile parts, bridge cables, etc.

425. Electric Refining of Steel. — Various types of furnaces are at present used for the refining of steel. Each type has some advantage over the other types. Electric

furnaces seem especially adapted to the production of high-grade steels from low-grade materials containing sulphur and phosphorus.

Heroult was first to construct a successful arc and resistance furnace for the refining of steel. The Heroult furnace (Fig. 181) has a capacity up to 15 tons of steel at a charge. Carbon electrodes are used. These cannot come in contact with the iron, since, at the temperature of the furnace, the carbon would rapidly enter into combination with the iron. In the Heroult furnace a basic lining is used and a basic slag covers the steel to be refined. The lower ends of the electrodes dip into the slag on top of the steel to such a depth that the current arcs through the slag to the iron underneath one electrode, passes through the iron to a point beneath another electrode, and then arcs from the iron through the slag to this electrode. The heat generated melts the furnace charge, and sulphur, phosphorus, and other acidic impurities are readily removed by the basic slag. When all the impurities have been removed, materials are added to bring the charge to the desired composition.

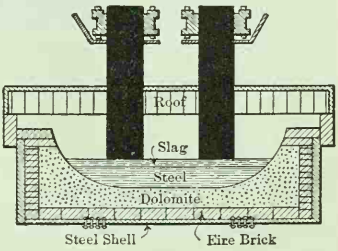


FIGURE 181.

The electric current passes through the slag. Due to the great resistance it meets, a high temperature results. The impurities of the melted iron are absorbed by the lining. This type of furnace is rapidly replacing the open hearth process.

426. Alloy Steels. — Certain of the less familiar metals when added in small quantities produce steels of great hardness, toughness, or tensile strength. More than 8%

of manganese, or chromium in smaller amount, gives great hardness to the steel. Tungsten and molybdenum are used in making *self-hardening* steels. Tools made from self-hardening steels retain a fine cutting edge without being tempered. For the cores of armatures and transformers, iron specially purified by the use of silicon is employed. This is called transformer iron, or *silicon steel*.

FIGURE 182.

A manual training high school student is tempering a piece of high carbon steel. When the steel is at precisely the right temperature it will be plunged into the pail of water.

Manganese, chromium, vanadium, and nickel steels are used for safes, armor plates, and parts of machinery subject to great stress or vibration, as shafts or automobile bearings. Deposits of iron ore that had been regarded as too refractory to work have been made valuable by the demand for these special steels because the ores contain these less common metals.

427. Tempering of Steel. — The process of varying the hardness of steel by heat treatment is termed *tempering* (Fig. 182). All steel contains iron carbide, Fe_3C, a very hard sub-

tance that readily dissolves in pure iron at a high temperature (above 670° F.). The hardness of a carbon steel depends upon the amount of iron carbide that is held in solution. When a carbon steel is heated the iron carbide enters into solution uniformly. When it is cooled *suddenly*, the iron carbide remains in solution, and a steel is obtained that is as hard as it is possible to obtain by heat treatment alone. If a solid solution of iron carbide in pure iron is cooled slowly, a change takes place below 670° F., and the iron carbide gradually passes out of solution and collects in small particles in the iron. We now have a mass of soft iron containing crystals of iron carbide, and the pure iron imparts the property of softness to the mass. The conglomerate of iron and iron carbide is far softer than the solid solution of iron carbide in iron. If a hard steel is heated to a temperature between 430° F. and 670° F., the iron carbide slowly separates from the solid solution and the mass is softened, that is, *tempered* by heat. The amount of iron carbide that separates depends upon the temperature and the length of time used in the heating. Thus the exact degree of hardness desired can be obtained.

Heating for a long time at moderate temperatures, or quick heating to the higher temperatures below 670° (the temperature at which iron carbide dissolves in iron) accomplishes the same result, viz. the separation of the iron carbide. The process, however, can be stopped at any time by a sudden cooling, and a steel of the desired hardness obtained. The temperature can be estimated by a play of colors, ranging from yellow to brown, red, purple, violet, and blue, to gray, which appear when the metal is heated. These colors are due to the formation of thin layers of iron oxide, causing interference colors. The colors follow each

other when the metal is cooled, and as soon as the right color is obtained the process is stopped by plunging the article into either water or oil.

Color	Temperature	Steel used for
Pale yellow	430° F.–450° F.	Razors
Full yellow	470° F.	Penknives
Brown	490° F.–510° F.	Shears and tools for brasswork
Purple	520° F.	Table knives
Blue	530° F.–570° F.	Watch springs and sword blades
Blue-black	610° F.	Saws and other wood-working tools

The yellow tints give very hard but brittle steels, while, as we proceed toward the blue, the steel is softer but tougher. The films are usually removed by grinding, but are seen on some saws and springs.

428. Classification of Iron and Steel. — Commercial iron is commonly classified as *cast iron*, *wrought iron*, and *steel*. Cast iron contains the highest percentage of carbon, wrought iron the least, and steel usually stands between. Chemical composition, however, is not a sure way of distinguishing these forms, as some steels contain less carbon than certain wrought irons. Moreover, the condition the carbon is in, whether free or combined with the iron, and whether iron carbide is segregated or is in solution, is a most important factor. The knowledge of the true nature of iron and steel has been largely gained by a careful study of the structure of a polished and etched section under a microscope and by the application of some principles recently developed by physical chemistry. At best, the classification of iron is difficult, and unless we classify a product according to the

process by which it is made, we shall be confused by the many varieties of steel and iron that grade into one another.

COMPARATIVE TABLE OF PROPERTIES

	Cast Iron	Wrought Iron	Steel	
			Low-carbon	High-carbon
Carbon, per cent	2% to 7.5%	0.05% to 0.3%	0.05% to 0.8%	0.8% to 2.0%
Melting point, approximate	1200° C.	1500° C.	1500° C.	1400° C.
Structure	Crystalline	Fibrous	Granular or fibrous	Granular
Hardness	Very hard	Soft	Moderately soft	Hard, if tempered
Possible treatment when heated	Can be cast, but neither welded nor tempered	Can be welded, but neither cast nor tempered	Can be cast and welded, but not tempered	Can be cast and tempered. Not easily welded
Uses	Castings, bases, and columns	Wire, electromagnets, and malleable iron	Structural steel, wire, nails, sheet	Tools, springs, permanent magnets

SUMMARY

The most common iron ores are hematite, Fe_2O_3, and limonite, $2\ Fe_2O_3 \cdot 3\ H_2O$.

Cast iron is produced in the blast furnace. The charge consists of iron ore, coke, and a flux material consisting of limestone or silica.

Slag is a glassy material that results from the combination of the flux with the impurities in the iron ore.

Wrought iron is produced in the puddling furnace, which is a reverberatory furnace. The charge is mainly cast iron and iron ore. Wrought iron is fibrous in structure and contains threads of slag throughout its mass.

Bessemer steel is produced in the Bessemer converter. The charge is melted cast iron; a lining, usually basic, acts as a flux in removing impurities. The essential parts of the operation are the burning out of carbon, silicon, and phosphorus. The oxides of the two last named elements are absorbed by the basic lining.

Open hearth steel is produced in a reverberatory furnace that is provided with a heat regenerating system. The charge is cast iron, scrap steel, and iron ore. The lining may be either basic or acidic. The oxygen for the removal of impurities is furnished by the iron ore. The lining acts as in the Bessemer converter.

Crucible steel is produced, in small quantities at a time, in graphite crucibles. The charge consists of wrought iron packed in carbon. The essential part of the operation is the absorption of carbon. For alloy steels, weighed quantities of the desired metals are added to the charge.

Electric furnaces are also used in producing high-grade steel on a large scale. The charge and the chemical operations resemble those of the open hearth furnace, but the heat is applied by an electric current passing through the high resistance of a slag. Tool steel is now produced by this method.

Welding is the process of joining two pieces by heating the surfaces to be joined until they soften, and then causing them to unite by pressure or by hammering.

Tempering is the varying of the hardness of a substance, nearly always steel, by heat treatment. The hardness of steel depends upon the amount of iron carbide the steel contains, and upon whether the iron carbide is separated or in solution.

For the composition and properties of various forms of iron and steel see the Comparative Table of Properties on page 435.

EXERCISES

1. Why does not iron occur to any extent in a free state?

2. Why was wrought iron probably the first form of iron worked by man?

3. When the coke is burned in the blast furnace, what becomes of the ashes that would ordinarily result from the combustion of coke?

4. Why is it necessary to produce slag in working a blast furnace?

5. What would be the constituents of a furnace charge for smelting an ore consisting of ferrous carbonate mixed with calcium carbonate? Explain.

6. Why cannot wrought iron be tempered?

7. What is the shape of the slag left when wrought iron corrodes? Is the slag left in the same shape when cast iron rusts away?

8. Why does the temperature of the Bessemer converter rise when cold air is blown through the cast iron in it?

9. For what purposes is Bessemer steel inferior to crucible steel? Why?

10. What kind of iron would you use for the manufacture of dynamo cores? Steam radiators? Bridge cables? Anchors? Springs? Chisels? Hammered iron work?

11. Why are the carbon electrodes of an electric furnace used for the refining of steel not permitted to dip into the molten iron?

CHAPTER XXXI

IRON AND ITS COMPOUNDS

429. Pure Iron. — Pure iron may be prepared by the reduction of pure iron compounds, as the oxalate, in a stream of hydrogen; or electrolytic iron may be deposited from solutions of certain iron salts. Pure iron is also obtained in an electric furnace operating in a vacuum.

Pure iron is a white, lustrous metal, which is very tough and which fuses only at a high temperature. It is malleable, ductile, and may be temporarily magnetized.

In dry air, pure iron does not rust, but in moist air rusting proceeds rapidly, particularly if carbon dioxide is present. Iron decomposes water very slowly at ordinary temperatures, but at higher temperatures the reaction proceeds rapidly. With cold, dilute acids, such as hydrochloric acid and sulphuric acid, hydrogen is evolved and a ferrous salt is formed. With hot concentrated sulphuric acid, certain reduction products may be produced. When cast iron is dissolved in acids, the unpleasant odor is due to the formation of hydrocarbons and to sulphur and phosphorus compounds from impurities in the iron.

430. Iron Ions. — Iron forms two kinds of ions,—bivalent, Fe^{++}, and trivalent, Fe^{+++}. Compounds in which iron has a valence of *two* are known as *ferrous* compounds; those in which the valence of iron is *three* are termed *ferric*

compounds. Bivalent ions result from the dissociation of ferrous compounds, and trivalent ions from the dissociation of ferric compounds.

431. Oxides of Iron. — *Ferrous oxide*, FeO, can be prepared by the reduction of ferric oxide with hydrogen or carbon monoxide. It is a black powder that cannot be kept in air on account of the ease with which it passes into ferric oxide.

Ferric oxide, Fe_2O_3, forms the most important ore of iron. It can be readily prepared by heating ferric hydroxide, ferrous carbonate, or ferrous sulphide. Ferric oxide constitutes the coloring matter of such pigments as Venetian red, Indian red, and light red. When ferrous sulphate is calcined (heated), a form of ferric oxide known as *rouge* is obtained. Rouge is used for polishing and as a pigment. Limonite, or hydrated ferric oxide ($2\,Fe_2O_3 \cdot 3\,H_2O$), is found in nature mixed with fine clay and sand. Such mixtures constitute the pigment *yellow ocher*. When calcined, various shades of yellow, orange, and brown are obtained. These are sold as raw sienna, burnt sienna, raw umber, and burnt umber.

The *magnetic oxide of iron*, Fe_3O_4, occurs in nature as magnetite. When found naturally magnetized, it is lodestone (Fig. 171). It is formed when ferric oxide is heated to a high temperature and when iron is burned in oxygen or in air. It constitutes what is known as blacksmith's scale, which is formed when red-hot iron is worked. When steam is passed over red-hot iron, hydrogen is liberated, and a firmly adhering film of magnetic oxide is deposited on the iron. This film prevents the rusting of the iron under it. *Russia iron*, used as a covering for locomotive boilers, etc.,

is iron that has been artificially coated with magnetic oxide of iron.

432. Hydroxides of Iron. — *Ferric hydroxide* can be formed by the addition of a base to a solution of a ferric salt:

$$FeCl_3 + 3\ NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3\ NH_4Cl$$

It is precipitated as a reddish brown, flocculent compound, which, on drying, changes to iron rust. *Iron rust* may be considered as a double compound of ferric oxide and ferric hydroxide, with a small proportion of ferrous bicarbonate. It is probably produced in a manner analogous to that described for the natural formation of hematite (§ 412). Iron dissolves in water in the presence of carbon dioxide, forming ferrous bicarbonate:

$$Fe + 2\ H_2CO_3 \longrightarrow Fe(HCO_3)_2 + H_2\uparrow$$

This oxidizes to iron rust:

$$4\ Fe(HCO_3)_2 + O_2 \longrightarrow Fe_2O_3 \cdot 2\ Fe(OH)_3 + H_2O + 8\ CO_2$$

The coating of rust does not protect the iron under it. On the contrary, it hastens the formation of additional rust, because, when the action is once started, carbon dioxide, the real cause of the rusting, is liberated in direct contact with the iron. Thus iron rust acts as a catalytic agent for its own formation.

When ferric hydroxide is heated to a red heat, it is converted into ferric oxide and water:

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$

Ferrous hydroxide, $Fe(OH)_2$, appears white when first precipitated, but soon changes to dull green and then to brown, by oxidation.

433. Chlorides of Iron. — *Ferrous chloride*, $FeCl_2$, is formed when iron is dissolved in hydrochloric acid in the absence of air. It can be crystallized as a pale green compound, $FeCl_2 \cdot 4\,H_2O$, unstable in air.

Ferric chloride, $FeCl_3$, can be prepared by passing chlorine over hot iron; by dissolving iron in aqua regia; and by dissolving ferric oxide in hydrochloric acid. When hydrogen peroxide is added to a solution of ferrous chloride containing hydrochloric acid, ferric chloride is instantly formed. Ferric chloride is commonly used when a soluble ferric salt is required, and as an astringent in medicine.

434. Change of Valence by Oxidation and Reduction. — The changes in valence that take place during certain reactions give an extended meaning to the terms *oxidation* and *reduction*, because such changes in valence are often brought about by the action of oxidizing and reducing agents. Hence the terms *oxidation* and *reduction* are often used to express change in valence. *Oxidation involves an increase in valence; reduction involves a decrease in the valence of some element.*

The terms oxidation and reduction are sometimes applied to reactions in which oxygen takes no part. If ferric chloride, $FeCl_3$, is treated with nascent hydrogen, ferrous chloride, $FeCl_2$, and hydrochloric acid are produced:

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

The iron atom is reduced from a valence of three in the ferric compound to a valence of two in the ferrous compound. By passing chlorine over heated ferrous chloride, the ferrous chloride is *oxidized* to ferric chloride, by the addi-

tion of an atom of chlorine, thus increasing the valence of the iron:

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

435. Sulphates of Iron.—*Ferrous sulphate*, $FeSO_4 \cdot 7\ H_2O$, is a by-product in many industries. Scrap iron is added to sulphuric acid that has been used in the refining of petroleum, or for cleaning iron. The iron is dissolved, and on evaporating the solution, crystals of green vitriol, sometimes called copperas, are obtained. Much ferrous sulphate is used in the manufacture of blue pigments, as a mordant, and in the preparation of black inks.

When solutions of ferrous sulphate and tannic acid are mixed, ferrous tannate, a nearly colorless compound, is formed. This is the chief ingredient of iron inks. As the writing would not at first be visible if a solution of pure ferrous tannate were used, some dye is added to give the ink color. On exposure to the air, ferrous tannate is changed to ferric tannate, which is insoluble, and has a black color.

Ferric sulphate, $Fe_2(SO_4)_3$, is formed when ferrous sulphate is oxidized in the presence of sulphuric acid. It is used with ammonium sulphate in the preparation of ferric ammonium alum, $NH_4Fe(SO_4)_2 \cdot 12\ H_2O$.

436. Removal of Ink Stains.—Iron ink stains may be removed by lemon juice or dilute oxalic acid, with subsequent treatment with an alkaline solution of sodium hypochlorite (Javelle water). The acid reacts with the iron compounds forming salts that are soluble in water. Ink may be washed out with water before it dries. If water does not take out the last trace, soak the cloth in sweet milk. Rust stains can be removed in the same way. It is difficult

to remove stains from silk, since any reagent that will take the stain out of the silk is likely to dissolve the goods.

437. Ferrocyanides. — On igniting a mixture of nitrogenous organic matter, scrap iron, and potassium carbonate, cooling the mass, and then treating it with hot water, *potassium ferrocyanide*, $K_4Fe(CN)_6$, passes into the solution. When the solution cools, crystals of potassium ferrocyanide, or yellow prussiate of potash, separate. These have a composition represented by the formula $K_4Fe(CN)_6 \cdot 3\ H_2O$.

A solution of potassium ferrocyanide does not give the usual characteristic reactions of iron because the iron exists as a part of a complex ion, $Fe(CN)_6^{----}$. When solutions of ferric salts and potassium ferrocyanide are brought together, a deep blue precipitate, ferric ferrocyanide, or Prussian blue, is formed. The reaction is made use of in testing for the ferric ions (Fe^{+++}):

$$4\ FeCl_3 + 3\ K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow + 12\ KCl$$

Prussian blue is an important pigment. Bluing, used for laundry purposes, sometimes contains Prussian blue. When clothes with which it is used are not thoroughly freed from soap, the alkali of the soap decomposes the ferric ferrocyanide, precipitating ferric hydroxide on the cloth and producing spots of iron rust:

$$Fe_4[Fe(CN)_6]_3 + 12\ NaOH \longrightarrow 3\ Na_4Fe(CN)_6 + 4\ Fe(OH)_3 \downarrow$$

438. Ferricyanides. — *Potassium ferricyanide*, or red prussiate of potash, $K_3Fe(CN)_6$, can be prepared by treating a solution of potassium ferrocyanide with chlorine:

$$2\ K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\ KCl + 2\ K_3Fe(CN)_6$$

Solutions of potassium ferricyanide, when added to those of ferrous compounds, give a blue precipitate, ferrous ferricyanide, or Turnbull's blue:

$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 \longrightarrow 6\ KCl + Fe_3[Fe(CN)_6]_2$$

439. Blue Prints owe their color to the formation of Turnbull's blue.

When a solution containing ferric chloride and a reducing agent, such as oxalic acid, is exposed to the sunlight, the ferric salt is reduced to a ferrous salt:

$$2\ FeCl_3 + H_2C_2O_4 \longrightarrow 2\ FeCl_2 + 2\ CO_2\uparrow + 2\ HCl$$

When a sheet of paper is coated in a darkened room with such a mixture, dried, and then exposed under a negative to the sunlight, the greatest reduction will take place where the light is brightest. On covering the exposed paper with a solution of potassium ferricyanide, Turnbull's blue will develop wherever there is any ferrous iron, and the depth of color will depend on the amount of ferrous salt present. In other words, potassium ferricyanide is in this case used as a developer. Where the paper has been protected from the light, the materials are unchanged. The picture can be fixed by washing away the ferric chloride and the excess of potassium ferricyanide.

In making commercial blue-print paper, a single compound, ammonium ferric citrate, serves both as the ferric salt and as the reducing agent. The paper is coated with a mixture of ammonium ferric citrate and the developer, potassium ferricyanide. Such a paper, after exposure, is both developed and fixed by simply washing with water.

SUMMARY

Pure iron is light gray, malleable and ductile.

Atomic weight 56. Valence 2 or 3. Melting point 1505°.

Iron **corrodes** when exposed to moist air. Red hot iron decomposes steam. Iron **dissolves** in dilute hydrochloric and sulphuric acids with the evolution of hydrogen and the formation of a ferrous salt.

Iron forms **two series of salts.** Ferrous salts contain iron having a valence of 2, and ferric salts contain iron with a valence of 3.

The **common oxides** of iron are ferric oxide (Fe_2O_3) and the magnetic oxide of iron (Fe_3O_4).

Ferric oxide pure, or impure and hydrated, is used for several paint pigments.

Russia iron is iron coated with a layer of the magnetic oxide of iron.

Ferric hydroxide is formed when a solution of a base is added to a ferric salt.

Iron rust varies in composition but may be considered as a double compound of ferric oxide and ferric hydroxide. Iron is prevented from rusting by coating it with paint, enamel, or some metal that closely adheres to it. Zinc, tin, aluminum, and nickel are the metals most commonly used for this purpose.

Ferric chloride is the most common ferric salt.

Ferrous sulphate, green vitriol, is the most common ferrous salt. It is used in the manufacture of inks and paint pigments.

Yellow prussiate of potash is potassium ferrocyanide $K_4Fe(CN)_6$.

Red prussiate of potash is potassium ferricyanide, $K_3Fe(CN)_6$.

Blue prints are made on paper coated with a ferric salt, potassium ferricyanide, and a reducing agent.

An increase in valence is termed **oxidation.**

A decrease in valence is termed **reduction.**

EXERCISES

1. Which would have the higher melting point, pure iron or ordinary cast iron? What principle is illustrated by these melting points?

2. Is pure hydrogen formed when hydrochloric acid is added to cast iron? Explain.

3. Is ferrous sulphate, or ferric sulphate, formed when iron is treated with an excess of dilute sulphuric acid? Explain.

4. How would you convert ferrous chloride into ferric chloride? Ferric chloride into ferrous chloride? Write the equations.

5. How would you determine whether a solution contained a ferric or a ferrous salt?

6. What chemical change takes place when ferrous sulphate is calcined? Mention important uses of the chemical compound that constitutes the residue.

7. Why is it difficult to keep a solution of ferrous chloride?

8. Which oxide of iron is used as a protective coating for iron? Which one accelerates the rusting of iron?

9. Briefly state the important changes that take place during the making of a blue print.

10. Give two definitions for oxidation. For reduction.

11. Which is involved in the conversion of ferrous sulphate into ferric sulphate, oxidation or reduction?

12. Name an acid suitable for removing iron rust spots from cotton cloth.

13. Why does the color of an iron ink change on exposure to air?

CHAPTER XXXII

COPPER AND ITS COMPOUNDS

440. Occurrence of Native Copper. — Copper is the only metal that occurs free in large, widely distributed deposits. For this reason, it was the first metal extensively used by man. The copper age followed the stone age. The

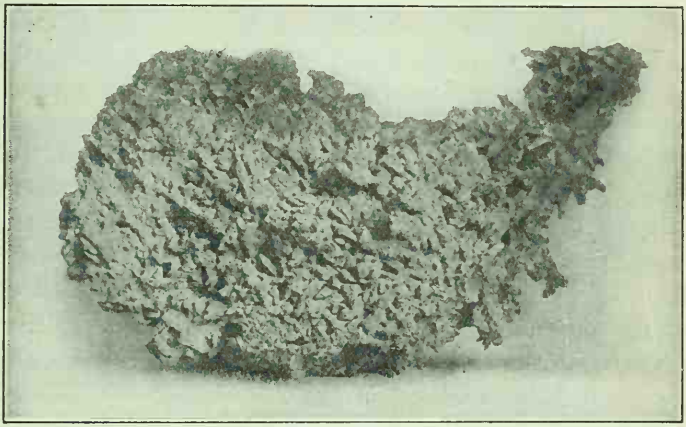


FIGURE 183.
This lump of native copper was found in a mine in northern Michigan. It measures 3 × 2 ft.

island of Cyprus was noted in the time of the Romans for its production of copper or Cyprian brass. We obtain the symbol Cu from the Latin name, *cuprum*.

The noted mines of native copper in Michigan, along the southern shore of Lake Superior, were extensively worked before Columbus discovered America. From them

masses of copper of enormous size, one of which weighed nearly five hundred tons, have been obtained. These mines are still an important source of copper.

441. Ores of Copper. — These are numerous, and many of them have a composition represented by complex formulas; the more important ores besides native copper contain sulphides, oxides, carbonates, and silicates. Much copper is obtained from an ore named chalcopyrite, the composition of which corresponds approximately to the formula $Cu_2S \cdot Fe_2S_3$. The mineral malachite, a basic carbonate of copper, $CuCO_3 \cdot Cu(OH)_2$, is of interest, because polished slabs of malachite often exhibit variegated patterns of different shades of green which are of great beauty, and are highly valued for ornamental purposes.

442. Metallurgy; Steps in Process. — The metallurgy of copper is usually complex; not only does the process vary with the kind of ore used, but similar ores, in different localities, are seldom treated in the same manner. Ores that contain native copper are crushed and washed to remove the impurities. The concentrated mass is then smelted and refined to obtain the copper. Ores consisting of compounds of copper other than the sulphides are reduced with carbon. There is usually a flux in the furnace charge. In case the ore contains much chalcopyrite, the process, as carried out by one of the large copper companies, consists essentially in:

1. Removal of a *portion* of the sulphur by roasting.
2. Elimination of the earthy material and the production of a complex sulphide, *matte*.
3. Production of impure copper, known as *blister copper*, from the *matte*.

4. Partial purification of the copper by a process known as *poling*.

5. Refining by electrolysis.

443. Roasting of Ore. — When chalcopyrite, $Cu_2S \cdot Fe_2S_3$, is roasted, the following reactions probably take place:

$$Fe_2S_3 + 4\,O_2 \longrightarrow 2\,FeO + 3\,SO_2$$
$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$$

444. The Production of Matte. — The roasted ore is then smelted in a blast furnace for the production of matte. The charge for the furnace consists of the roasted ore, some unroasted (green) ore, and coke. The copper oxide of the roasted ore reacts in the furnace with the iron sulphide of the unroasted ore, producing cuprous sulphide and iron oxide:

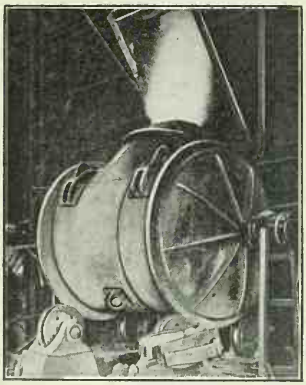
$$3\,Cu_2O + Fe_2S_3 \longrightarrow 3\,Cu_2S + Fe_2O_3$$

The copper is converted into a sulphide, since copper has a greater tendency to unite with sulphur than have any of the other metals in the ore. The silica in the ore unites with the iron oxide to form a glassy slag. The essential product of the roasting is *matte*, which is mainly cuprous sulphide with an impurity of ferrous sulphide.

The matte and slag are run into a shallow tank, called a forehearth, where the lighter slag, rising to the top, flows off, while the heavier matte is drawn off at the bottom. The matte, in addition to the cuprous and ferrous sulphides, contains all the gold and silver of the ore, and generally arsenic and antimony. The percentage of copper in matte varies from 45% to 60%.

445. Conversion of Matte to Blister Copper. — The melted matte is poured into a converter similar to that used

for the production of Bessemer steel (Fig. 178). Air is blown through the molten mass (Fig. 184), and oxidizes the sulphur, iron, and other impurities. Those oxides that are volatile are driven off. The iron oxide, however, unites with the silicon dioxide of the furnace lining to form a slag. The copper thus obtained still contains all of the gold and silver present in the original ore, and small quantities of other impurities. Molten copper dissolves considerable sulphur dioxide, which is expelled when the mass cools, giving the copper an appearance which causes it to be called *blister copper*.



Courtesy of the Scientific American.

FIGURE 184.

A Bessemer converter, lined with silicon dioxide, that is used to separate iron and sulphur from copper in the treatment of chalcopyrite ore.

The same result is obtained by heating matte in a reverberatory furnace similar to that used in the next operation, and allowing the sulphur to be oxidized by the air passing over it.

446. Poling of Blister Copper and Casting of Anode Plates.— Blister copper is melted in a reverberatory furnace (Fig. 185), and is stirred and reduced by the hydrocarbon gases liberated when a long pole or log of green wood is forced into the metal. This process, called *poling*, has for its object the reduction of the small amount of copper oxide that is present to metallic copper. Any one who has seen the interior of a poling furnace in operation will retain a vivid impression of the seething mass of molten copper, dazzling in its brilliancy of color.

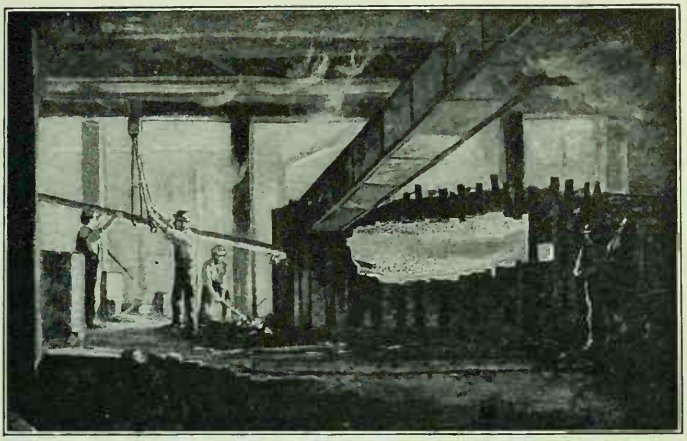


FIGURE 185.

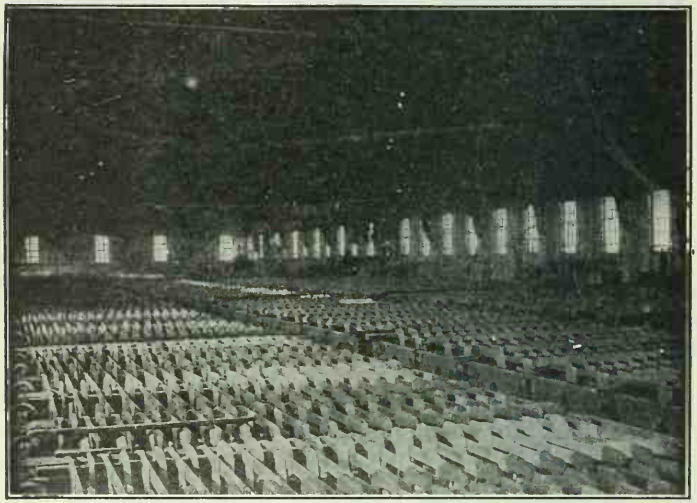
The trunk of a freshly cut tree is thrust into molten, impure blister copper in this reverberatory furnace. The escaping sap makes the copper seem to seethe and boil. The carbon and hydrocarbons of the decomposing wood reduce the oxides of the metals that are present.

447. Refining by Electrolysis. — After being poled, the copper is cast into anode plates to be refined by electrolysis. These plates are suspended in wooden tanks containing a warm solution of copper sulphate acidulated with sulphuric acid (Fig. 186). When the current passes, pure copper is transferred from the anode to the cathode plate, placed a short distance from it. During the electrolysis the solution is kept slowly circulating, and at a definite concentration. A part of the impurities enter the bath, while others, including gold and silver, fall to the bottom of the tank and form a substance known as *mud*. The gold and silver are recovered from the mud.

448. Properties of Copper. — Copper has a characteristic reddish color. Only two of the common metals, gold and

silver, surpass it in malleability and ductility. It stands next to silver as a conductor of electricity.

On exposure to the atmosphere, copper is attacked by carbon dioxide in the presence of moisture, and becomes covered with a coating of a basic carbonate of a greenish color. The coating, once formed, adheres to the copper



Courtesy of the Scientific American.

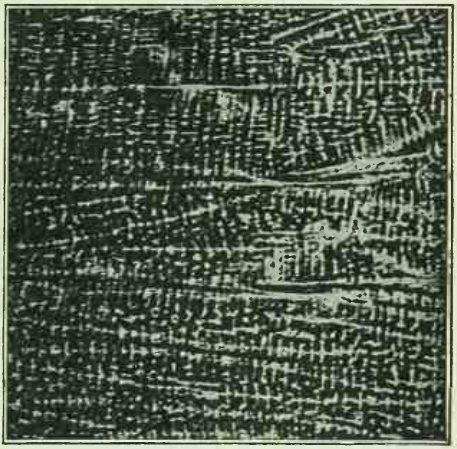
FIGURE 186.

Many hundreds of pairs of impure anode and pure cathode plates are suspended in the warm solution of copper sulphate and sulphuric acid which these tanks contain. The current carries pure copper from the anode to the cathode plate, and impurities, including gold and silver, are deposited at the bottom of the tank.

underneath and protects it. Copper is readily attacked by nitric acid (preparation of nitric oxide, § 253), but neither dilute hydrochloric acid nor dilute sulphuric acid attacks it in the absence of air. It is readily acted upon by hot, concentrated sulphuric acid. Boiling concentrated hydro-

chloric acid slowly converts copper into cuprous chloride, CuCl.

449. Uses of Copper. — Much copper is employed in the manufacture of alloys. *Brass* is an alloy of copper and zinc; *bronze* (Fig. 187) is an alloy of copper and tin, to which sometimes zinc and other metals are added; the one-cent piece is a typical bronze. *German silver* is an alloy of copper, nickel, and zinc; and *aluminum bronze* is an alloy of copper and aluminum. Copper is also used in the manufacture of various articles for domestic and scientific purposes, such as water heaters, kettles, stills, vacuum pans, etc.



Courtesy of the Cleveland Dental Mfg. Co.

FIGURE 187.

A micro-photograph which reveals the structure of a copper-tin alloy. The crystals have a definite composition of copper and tin.

The most important use of copper, however, is for wires and cables for the transmission of electric currents. For this purpose it must be practically pure, as very small amounts of impurity considerably impair the conductivity. If the conductivity of pure copper is considered as 100, copper containing 0.8% of arsenic has a conductivity of only 30, and copper containing 0.5% of silicon has a conductivity of 28.

450. Compounds of Copper. — Copper forms two kinds of ions, cuprous (Cu^+), and cupric (Cu^{++}). The univalent cuprous ion unites with negative ions to form cuprous compounds, while the divalent cupric ion forms cupric compounds.

	Oxide	Sulphide	Chloride
Cuprous	Cu_2O	Cu_2S	$CuCl$
Cupric	CuO	CuS	$CuCl_2$

451. Oxides of Copper. — *Cuprous oxide*, or red oxide of copper, Cu_2O, occurs in nature. The dull red color of unpolished copper is largely due to cuprous oxide. When a strip of copper is heated in air, a layer of cuprous oxide may be found under the layer of black cupric oxide. If a mixture of cupric oxide and charcoal is heated, the cupric oxide is first reduced to cuprous oxide, and then the cuprous oxide is reduced to copper. Other reducing agents have a similar effect on cupric oxide.

Cupric oxide, or black oxide of copper, CuO, can be prepared by heating copper in air. Many compounds containing hydrogen are oxidized when heated with cupric oxide, the hydrogen being converted into water. If carbon is present, it is converted into carbon dioxide. These facts make cupric oxide a valuable substance to use in the determination of the quantity of hydrogen and of carbon present in compounds containing these elements.

452. Preparation of Copper Sulphate. — Crystallized copper sulphate, or blue vitriol, $CuSO_4 \cdot 5\,H_2O$, is prepared on a large scale by placing coarse copper shot in a perforated lead basket (Fig. 188), and then causing the basket and contents to move up and down so that they will at one

time be in the air and at another time immersed in warm, dilute sulphuric acid. When the basket enters the acid, air is carried into the acid with the shot. The action of the acid on the copper in the presence of air results in the formation of copper sulphate, which passes into solution:

$$2\,Cu + O_2 + 2\,H_2SO_4 \longrightarrow 2\,CuSO_4 + 2\,H_2O$$

The solution, after being sufficiently concentrated, is allowed to stand in lead-lined vats in which are suspended lead strips. Blue vitriol crystallizes on the lead and is purified by recrystallization.

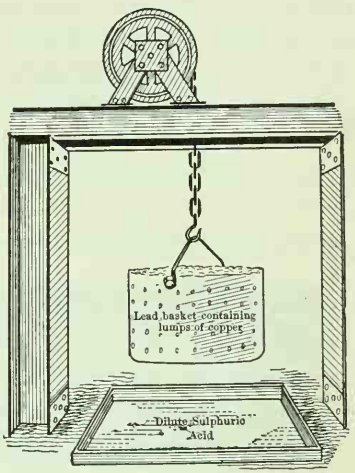


FIGURE 188.

How copper sulphate is made commercially. The lead basket moves slowly up and down. The copper, moistened with dilute sulphuric acid, is first exposed to the oxidizing action of the air, and then enters the acid, carrying air with it. Thus, with the aid of the oxygen of the air, dilute sulphuric acid dissolves the copper.

Blue vitriol is also obtained as a by-product in one method used in separating gold from silver. The melted alloy of these two metals is granulated by pouring it into cold water. The granulated mass is boiled with concentrated sulphuric acid until the silver is dissolved as silver sulphate. The gold remains undissolved and settles to the bottom of the vat. The solution of silver sulphate is removed to lead-lined vats and the silver is separated by the addition of copper:

$$Ag_2SO_4 + Cu \longrightarrow CuSO_4 + 2\,Ag\downarrow$$

453. Properties and Uses of Copper Sulphate. — Copper sulphate crystallizes from water solutions and forms deep blue crystals (Fig. 189) that effloresce in dry air. Its water solution gives an acid reaction with litmus (§ 187).

For some time the great value of copper sulphate as a fungicide has been recognized. A mixture of copper sulplate and slaked lime, known as the Bordeaux mixture, is now extensively employed for this purpose. A thick paste of calcium hydroxide and copper sulphate was first used near the city of Médoc, France, to keep boys from stealing grapes. When placed upon the trellises and vines

FIGURE 189. — A MASS OF COPPER SULPHATE CRYSTALS.

it was conspicuous, and was believed to be poisonous. In 1882, Millardet, professor of botany in Bordeaux, visited the vineyards near Médoc, and was informed by the grape growers that those portions of the vineyard that had been treated with the paste were not attacked by mildew. Much work has been done in the United States Department of Agriculture in determining the value of the Bordeaux mixture as a general fungicide. Its use in this country has saved crops worth many hundreds of thousands of dollars.

Dilute solutions of copper sulphate are used to moisten seeds of cereals prior to sowing, to prevent the attack of fungi called smuts.

Plants known as algæ grow abundantly in the water of ponds and reservoirs. Some of them impart to the water disagreeable odors; others produce effects equally undesirable. Copper sulphate is added to the water of ponds thus affected, in the proportion of one part of copper sulphate to from one to eight million parts of water, for the purpose of destroying algæ. The solution is too dilute to kill fish. The copper sulphate appears to react with the albumen of the algæ to form an insoluble substance which sinks to the bottom of the ponds.

Copper sulphate has many other important uses. It is employed in batteries, in electroplating, as a mordant in dyeing, and for making other compounds of copper.

SUMMARY

The atomic weight of copper is 63.6; specific gravity 8.9; melting point 1083° C.

Copper occurs native; this and the sulphides are its principal sources.

It is separated from its ores by burning out the sulphur and reducing the oxide by carbon. It is purified by electrolysis.

Copper is durable under ordinary atmospheric conditions, and is used for protective coverings. Being ductile and a good conductor, it is used for electric conductors. Commercial **alloys** containing copper are brass, bronze, German silver, and aluminum bronze.

Copper sulphate is the most important compound of copper. It is used as a fungicide, for paints, for plating, and in some batteries.

EXERCISES

1. What metals are usually found associated with copper?
2. How is iron separated from copper? How is silver?

3. Heavy electric cables of copper often have iron wire above them to which they are fastened. Why?

4. What is the result of the action of atmospheric agents on copper?

5. What volume of nitric oxide will be produced by the action of 10 grams of copper with nitric acid?

6. How could you tell whether a given substance was gilt (brass) or gold?

7. What is the most important use of copper? How does its purity affect its fitness for this purpose?

8. Name three alloys of copper and their constituents.

9. What copper compound is used to destroy fungi? Why?

10. What would be obtained if ammonia were passed over heated copper oxide?

11. How much blue vitriol could be obtained from one ounce of copper?

12. How much copper could be obtained from one ounce of blue vitriol?

13. Write the equation for the change that takes place when a strip of copper is placed in a solution of silver nitrate.

14. One gram of silver is obtained by the decomposition of its sulphate by copper. What weight of copper passes into solution?

15. Calculate the percentage of water of crystallization in crystalline copper sulphate, $CuSO_4 \cdot 5\ H_2O$.

16. State two uses for copper sulphate.

17. How could you tell whether or not a given substance is a compound of copper?

18. Outline the process by which a vessel might be copper plated.

19. Account for the greenish color of the Statue of Liberty.

CHAPTER XXXIII

SILVER, GOLD, AND PLATINUM

Silver

454. Occurrence. — Silver is the most common of the precious metals. Silver has been known from the earliest times, as it frequently occurs free in rocks from which it is easily separated.

Native silver is found in Arizona, Mexico, South America, and elsewhere, but much of the silver now used is obtained from sulphide ores, usually associated with lead, copper, arsenic, and gold. Silver chloride (horn silver) occurs in nature, and traces of silver compounds are found in sea water. The principal supply of silver is from Mexico, United States, Canada, Australia, and Peru.

455. Metallurgy. — The ores of silver are so numerous and complex that various processes are employed in the separation of the metal, but since so large a proportion of the commercial metal is obtained from lead ores, only the method used for these (Parkes' process) will be described.

The ore, largely lead sulphide, is roasted to remove sulphur, and then reduced as described under the metallurgy of lead (§ 498). The crude metal thus obtained is heated in a reverberatory furnace and stirred. Such metals as copper, antimony, and arsenic are oxidized, forming a

scum on the surface of the lead, and this is skimmed off. The molten metal is next run into iron pots and a small percentage of zinc is stirred into it. As the mixture cools, an alloy of zinc with silver and gold comes to the top in lumps, which are removed. Little of the lead is taken out, because lead and zinc do not readily alloy. If there is much silver in the crude lead, the treatment with zinc may be repeated.

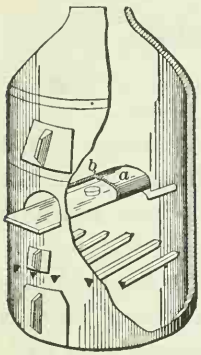


FIGURE 190.

The small, bone-ash dish (*b*) contains the alloy which is being cupelled. Only silver and gold resist the oxidizing action.

The alloy of zinc, lead, silver, and gold is now heated in a retort and the zinc removed by distillation.

The residue, containing lead, silver, and gold, is then *cupelled*, that is, heated in a bone-ash dish in a shallow furnace exposed to the air. The lead oxidizes, and the melted lead oxide flows off and is recovered. The melted silver and gold that remains is then poured into molds. A small cupellation furnace is shown in Figure 190; *a* is a muffle and *b* the cupel in which the silver and gold is finally left as a metallic button.

The gold is separated from the silver by treating the alloy with hot concentrated sulphuric acid or nitric acid. The silver dissolves as the sulphate or the nitrate, but the gold is not affected, and after washing is melted and cast into bars.

The silver is recovered from the solution by hanging in it plates of copper:

$$Ag_2SO_4 + Cu \longrightarrow CuSO_4 + 2\,Ag\downarrow$$

The silver is deposited in a fine crystalline form known as

cement silver. The "silver tree" (Fig. 191) is produced in this way.

Another method of separating gold from silver is by electrolysis. The alloy is made the anode in a dilute nitric acid solution of silver nitrate, the anode sheet being inclosed in a canvas bag. With a current of low voltage, silver is dissolved from the anode as the nitrate and redeposited on the cathode as practically pure metal. The gold is unaffected and remains at the anode, and as the anode disintegrates, collects as a mud in the canvas bag.

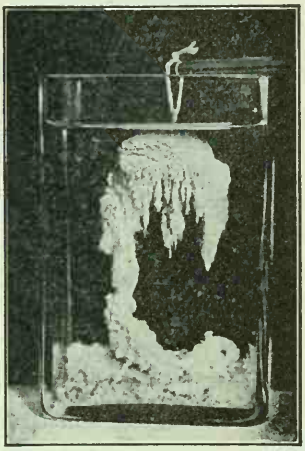


FIGURE 191.

A tree of silver! It was produced by the replacement action that occurs when copper is put into a solution of silver sulphate.

456. Physical Properties. — Silver is a white metal, fairly hard, capable of receiving and retaining a high polish. It is the best conductor of heat and electricity. Being ductile and malleable, it is readily worked into articles of various shapes.

457. Chemical Properties. — Silver does not change in pure air and does not oxidize on being heated. It darkens readily in the presence of sulphur compounds, showing such stains as are seen on silver spoons that have been used with eggs or mustard, on coins carried in the pocket, or on silverware about the house. "Oxidized" silver owes its color to a thin coating of silver sulphide, produced by dipping the metal in a solution of crude potassium sulphide.

Alkalies do not affect silver. Nitric and sulphuric acids react with it as they do with copper:

$$2\,Ag + 2\,H_2SO_4 \longrightarrow Ag_2SO_4 + 2\,H_2O + SO_2\uparrow$$
$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + 2\,H_2O + NO\uparrow$$

458. Cleaning Silverware. — The tarnish may be removed from silver by rubbing with a very fine abrasive, like diatomaceous earth (electrosilicon), or by dissolving it chemically. Moistening a dry silver polish with ammonia aids its action, on account of the solvent power of the ammonia. The cyanide solution used by jewelers should never be employed in the home, as it is one of the most deadly poisons known. There has been devised a simple and very satisfactory method of cleaning silverware by boiling it in an aluminum dish with water containing a little baking soda. The combination constitutes a voltaic cell in which aluminum forms one plate, silver the other, and the soda solution the electrolyte. A feeble current is generated which tends to liberate hydrogen at the silver. This acts on the silver compounds that form the tarnish and removes them. In cleaning plated silver, the fact that the plating is pure silver, and is, therefore, softer than ordinary sterling or coin silver should be kept in mind. Plated silver should never be rubbed hard with abrasive polishes, even those which might be suitable for solid silver.

459. Uses of Silver. — Since pure silver is not hard enough to stand the wear and tear of constant use, it is alloyed with other metals, for instance copper. The silver coins of the United States contain 90% of silver and are said to be 900 fine. British coins are 925 fine (92.5% silver),

and this is the grade known as *sterling silver*. On account of its color, durability, and luster, silver has long been used for jewelry and ornaments, and as a plating on cheaper metals.

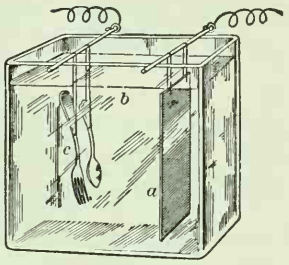


FIGURE 192.

(*a*) is a silver anode ; the fork and spoon form the cathode.

Mirrors are made by depositing a layer of silver on polished glass. A solution of silver nitrate to which has been added some ammonia and a reducing agent, as formaldehyde or grape sugar, is flowed over the glass and gently warmed. The silver is reduced and deposited as a bright film on the glass. This is washed, dried, and varnished to protect it.

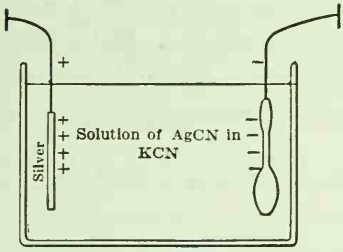


FIGURE 193.

The movements of the ions result in producing a thin, even coating of silver on the brass spoon (cathode), and in an action at the anode by which the silver bar dissolves, forming silver cyanide.

460. Silver Plating is usually done by electrolysis. To secure a firm, uniform deposit, the electrolyte is a solution of silver and potassium cyanides (Fig. 192, *b*) made by adding potassium cyanide solution to a solution of silver nitrate until the precipitated silver cyanide is dissolved. A bar or sheet of silver is used as the anode (*a*) and the object to be plated as the cathode (*c*), a rather weak current being employed. The positive silver ions are discharged and deposited on the cathode. The negative cyanide ions, discharged on the anode, combine

with the silver, forming silver cyanide. This, on dissolving, is dissociated. The amount of silver in the solution is unchanged, for silver is dissolved from the anode and deposited on the cathode.

461. Compounds of Silver. *Silver nitrate*, $AgNO_3$, is the most common compound. It is prepared by dissolving silver in nitric acid:

$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + 2\,H_2O + NO\uparrow$$

It is very soluble in water and crystallizes from it in flat, rhomboidal, transparent crystals. In contact with organic matter and exposed to the light, it darkens. Molded into sticks, silver nitrate is used as a cauterizing agent for warts, wounds, and sores, and is known as *lunar caustic*. Silver nitrate is used in indelible inks, and the black mark they produce is due to silver reduced from the nitrate. Silver nitrate is the most important compound of silver, because most of the other silver compounds are made from it.

Silver chloride, AgCl, is made by adding a solution of a chloride to a solution of a silver salt:

$$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO_3$$

The silver chloride separates as a white, curdy, insoluble solid. Silver chloride does not dissolve in acids, but dissolves in ammonia and in sodium thiosulphate, the *hypo* of the photographer.

Silver bromide, AgBr, and *silver iodide*, AgI, resemble the chloride; they have a yellowish tinge, are more easily changed in the light, and are less soluble. Like the chloride, they are extensively used in photography.

Photography

The preparation of the photographic negative involves four processes: the exposure, the development, the fixing, and the washing.

462. Exposure. — The photographic plate consists of glass or transparent celluloid coated with a film of gelatine containing very finely divided silver bromide, which, as has been stated, is *sensitive* to light in that it becomes *more easily reduced.* The presence of gelatine in the mixture aids by rendering the silver bromide more sensitive than it would otherwise be; this is due to the fact that gelatine readily absorbs bromine. It is probable that the light reduces to metallic silver a minute, invisible quantity of the silver bromide.

In the camera, an inverted image of the object is thrown on the plate. This image is composed of light and dark spots. Where there is light, a slight reduction of silver bromide occurs; where there are dark spots the silver bromide remains unaltered. The change, however, is not apparent in any way until the plate is put into the developer.

463. Developing. — *A developer is an alkaline solution of a weak reducing agent, of such strength that it affects the silver bromide in a noticeable degree only in those spots where the reduction has already been started by the action of light during the exposure.* When put into the developer, the plate soon begins to show black spots of metallic silver in places that were most strongly acted on by light.

$$2\,AgBr + H_2O \longrightarrow 2\,Ag + 2\,HBr + O$$

Ferrous sulphate, pyrogallol, hydroquinone, and many other reducing agents are used as developers. The acid is

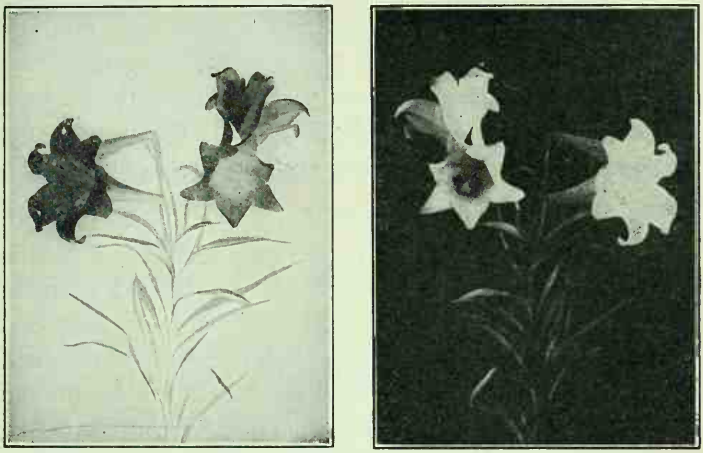
neutralized by the alkali added in the developer, and the oxygen is removed by the reducing agent. The developer takes up the oxygen represented in this equation.

464. Fixing. — If left in the developer long enough, the entire plate would become black. At the right point, therefore, the development must be stopped by transferring the plate to the fixing bath. The *fixing bath* is a solution of sodium thiosulphate, $Na_2S_2O_3$, commonly called *hypo*. It is capable of dissolving many silver *compounds*, such as the silver bromide, but has no effect on metallic silver. The purpose of the fixing bath, therefore, is to remove from the gelatine emulsion all unreduced silver bromide. When this has been accomplished the plate is no longer sensitive to light.

On the fixed plate, those parts of the scene which are brightest, that is, those parts which are white or blue, are represented by a dark deposit of silver; the dark parts of the scene are clear, so that shades are reversed; hence it is called a *negative* (Fig. 194, *a*). It contains colloidal silver suspended in gelatin.

465. Printing and Toning. — The finished picture on paper is made from the negative. The paper is *sensitized*, as was the plate, by a film of silver chloride or bromide. It is exposed to the light under the negative. Now those parts of the paper under the clear parts of the negative will be affected most by the light, and will be the darkest on reduction; the parts under the heavy deposits will be little affected, and will appear light, as they do in the object, so that the print, being the reverse of the negative, is a *positive* (Fig. 194, *b*). Its shades agree with those of the object photographed.

The positive is developed in the same manner as the negative in most cases, but in *printing out* papers, the developer is in the paper, so that the reduction occurs and the picture appears during the exposure. The print is fixed and washed as the plate was. To render them more permanent and to improve the color, prints are some-



a *b*

FIGURE 194.

The first picture shows a photographic negative. The lilies appear black because light, on striking the plate, initiated an action which was completed by the developer and resulted in the production of finely divided silver.

times *toned* by immersing them in a solution of gold chloride, so that some of the silver of which the pictures are composed is replaced by gold, giving it a warmer tone. Platinum and lead compounds are also used in *toning*. Other materials besides silver compounds might be used, but these are the most sensitive to slight variations in light and are the most easily controlled. The blue print process is described in § 439.

Gold

466. Occurrence. — Gold has been known from the earliest times. At present the principal supply comes from Africa, the United States, and Australia. It commonly occurs native, or alloyed with silver and other metals. It also occurs combined with tellurium, an element closely related to sulphur. Native gold is found in veins running through quartz rock and also in the beds of streams whose sands have been formed from the disintegration of such gold-bearing quartz. It has been found in nuggets varying in size from that of a tiny pebble to a mass weighing over a hundred pounds.

467. Separation. — From river sands and gravel gold is separated by washing with water. The lighter rock particles are washed off, leaving the gold. Partially disintegrated rock and coarse gravels are sometimes mined by dredging, crushing, and washing them with streams of water through troughs lined with coarse cloth. These cloths retain the heavy gold and permit the soil and gravel to be swept on.

468. Metallurgy. — When gold occurs in veins in massive rock, the rock is blasted with dynamite. The broken rock is crushed to small pieces by powerful iron crushers and is then pounded into fine powder by heavy iron stamps working in iron troughs. Water is kept flowing through these troughs, and the gold and rock leave them as a thin mud. This is caused to flow over silver-plated copper plates coated with mercury. The mercury amalgamates with the gold, and when a sufficient quantity accumulates, the amalgam is scraped off the plates and freed from mercury by distillation.

The gold that escapes amalgamation is extracted by means of sodium cyanide. The mud is allowed to stand in a weak solution of cyanide exposed to air for days or weeks and a double cyanide of gold and sodium is formed. The gold is precipitated from this solution by zinc or is extracted by electrolysis. This cyanide process is also applied directly to ores poor in gold and to tellurides. Its use in this country is increasing.

The separation of gold from copper slimes has already been mentioned (§ 447).

469. Properties. — Gold is soft and heavy and is the most malleable and one of the most ductile of metals. The presence of a small amount of other metals, however, often makes it brittle. Gold leaf has been made $\frac{1}{250000}$ of an inch thick. Gold leaf transmits green light. Suspensions of very finely divided gold are known as *colloidal suspensions*. Their color, which depends on the size of the particles, varies from red through purple to black.

Gold is unaffected by air or water at any temperature. Ordinary acids do not act on it, but it is dissolved by *aqua regia*, with the formation of auric chloride, $AuCl_3$.

470. Uses. — Pure gold is used as gold leaf. The metal is too soft to be used alone for other purposes and is alloyed with silver or copper. The proportion of gold is always indicated by the number of carats fineness: pure gold is 24 carats fine, 18-carat gold contains 18 parts by weight of gold and 6 parts of other metal. This carat should be distinguished from the carat used in weighing gems, which has recently been standardized at a weight of 200 milligrams. The gold coins of the United States are 90% gold and 10%

copper. Articles are gold plated by an electroplating process, using a bath of double cyanide of gold and potassium.

Platinum

471. Occurrence. — Platinum, alloyed with osmium and iridium, which closely resemble it, and with other metals, occurs native. The most important deposits of platinum are in the Ural Mountains; it is also found in California, Alaska, Australia, and a few other places. The separation of platinum from the metals alloyed with it is a complicated process.

472. Properties. — Platinum is a white, lustrous metal, about twice as heavy as lead. It is very malleable and ductile and is infusible except in the oxyhydrogen flame or the electric arc. When hot, it condenses on its surface, or *adsorbs*, large quantities of hydrogen with an increase in temperature, and releases the hydrogen on cooling. It does not take up oxygen when hot, but condenses it on the surface when cold. Platinum may be obtained as a fine black powder, *platinum black*, by the action of a reducing agent on a solution of one of its salts and as a *spongy platinum* by igniting the double chloride of platinum and ammonium. Platinum black as a catalytic agent produces a maximum effect for the money invested, on account of the large surface it possesses in proportion to its mass.

Platinum is not attacked by air or water at any temperature, and is not affected by acids, except *aqua regia*. Caustic alkalies, phosphorus, silicon, and carbon attack it when hot, so none of these substances should be heated in platinum vessels. Platinum should never be heated in a smoky flame, because platinum carbide is formed and the

vessel is disintegrated; nor should metals be heated in platinum vessels.

473. Uses.— The infusibility of platinum and its chemical indifference toward the great majority of elements and compounds render it invaluable in chemical operations. It finds extensive use in the laboratory, in the form of dishes (Fig. 195), wire, and foil. On account of its cost, which is now much more than that of gold, it is used only to a limited extent in chemical manufactures. The great expense, however, is partly compensated for by its indestructibility. Large quantities of platinum are employed as a catalytic agent in the manufacture of sulphuric acid by the contact process, and in the oxidation of ammonia as a step in the manufacture of nitric acid. It is a good conductor of electricity and expands with heat at the same rate as glass. Its alloy with iridium

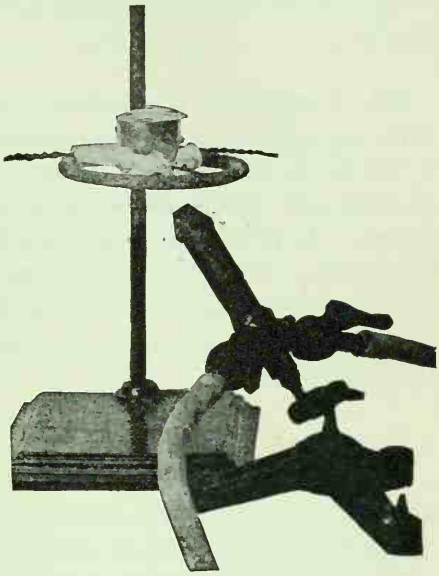


FIGURE 195.

Platinum serves well for chemists' crucibles because it will not melt at any temperature obtained by burning illuminating gas in air, as in the blast lamp. Platinum resists the action of acids, but not that of alkalies.

is hard and unalterable in air and is used for the manufacture of government standards of length, and this alloy, under the name of *hard platinum*, is used in most platinum ware. A considerable amount of platinum is used in settings for jewels. This is unfortunate, as much platinum needed for industrial operations is thus withdrawn from the market.

474. Compounds of Platinum. — The most important platinum compound is *chloroplatinic acid*, H_2PtCl_6, which is formed by dissolving platinum in *aqua regia*. Chloroplatinic acid forms chloroplatinates with metallic compounds. It is used in toning platinotypes and as a test for potassium compounds. The test depends upon the fact that potassium chloroplatinate is but slightly soluble in water or alcohol, while the corresponding sodium compound is decidedly soluble.

SUMMARY

Silver occurs in nature as metallic silver, as the chloride, and with other metals in complex sulphides.

It is extracted from lead bullion by means of zinc, and purified by electrolysis or treatment with acid.

Silver has a specific gravity of 10.5; atomic weight 108; melting point 961°. It is the best conductor of heat and electricity.

Silver is **unaltered by pure air**, but is tarnished by sulphur compounds.

Silver is **alloyed** with copper for most uses. A double cyanide of potassium and silver is used for **electroplating.**

Silver nitrate is made by dissolving silver in nitric acid. It is used in making other silver compounds.

The **compounds of silver with the halogens** are insoluble. They are made more easily reducible by the action of light. **Photo-**

graphic plates are coated with silver bromide, which, after exposure to the light, can be reduced by a developer. The unreduced silver bromide is dissolved by sodium thiosulphate.

Prints are made by exposing to light, under the negative, paper coated with silver bromide or chloride. Toning is the replacement of the deposited silver of the print by gold or platinum.

Gold occurs native, and alloyed with silver and other metals.

It is separated by alloying it with mercury, or by dissolving it with cyanides.

Gold is the most **malleable** metal and is very **ductile.**

Gold has a specific gravity of 19.3; atomic weight 197; melting point 1062°.

It is unaltered by air or water, but dissolves in *aqua regia.*

Platinum occurs native, alloyed with similar metals.

It is unattacked by air, water, and acids, except *aqua regia.* Caustic alkalies, phosphorus, and some other elements attack it when hot.

Finely divided platinum is a powerful catalytic agent for certain purposes.

EXERCISES

1. Why does not silver occur as an oxide?

2. Give the use of zinc, the cupel, and the electric current in the extraction of silver from its alloys with lead.

3. How much metallic silver can be obtained from 10 grams of silver nitrate by simple replacement?

4. Why is not silver commonly used as an electric conductor?

5. What is the compound formed when silver tarnishes?

6. What gas much used in the qualitative laboratory discolors silver?

7. What is horn silver? "Hypo"? Sterling silver? Lunar caustic? Oxidized silver?

8. In what respect does coin silver differ from pure silver? How does "Sterling" silver differ from coin silver?

9. Compare the action of silver with concentrated sulphuric acid and that of zinc with dilute sulphuric acid.

10. What use is made in the laboratory of the insolubility of silver chloride? Write an equation for the preparation of silver chloride.

11. How much silver nitrate can be made from a dime weighing 2.45 grams?

12. Give the action of the developer, the fixing bath, and the toning solution in photography.

13. Why is it necessary to wash plates and prints for a long time after fixing?

14. Give two characteristic properties and two important uses of (*a*) gold; (*b*) platinum.

15. Why do gold and platinum occur chiefly in an uncombined condition?

16. Why should the use of platinum in jewelry mountings be prohibited?

17. What is meant by "18 carat" gold?

Charles Martin Hall (1863–1914) was the inventor of the electrolytic process by which aluminum is now produced. During his course in Oberlin College he became interested in aluminum and set about to find a cheap method of producing it. Failing in his attempts to use reducing agents, he turned to the electric current. His problem was to find a suitable solvent for aluminum oxide. He found that melted cryolite would serve this purpose, and after some preliminary difficulties, his process was established on a commercial basis. This process reduced the price of aluminum to about eighteen cents per pound. It is interesting to know that the same process was independently invented by Heroult in France. In March, 1911, Hall was awarded the Perkin Medal.

CHAPTER XXXIV

ALUMINUM AND ITS COMPOUNDS

475. Occurrence. — Aluminum never occurs in a free state, although it is one of the most abundant and widely distributed elements. Emery, corundum, the ruby, and the sapphire are more or less pure forms of aluminum oxide. Clay and the rocks by the decomposition of which it is formed, consist chiefly of aluminum silicate. Two minerals of great importance in the preparation of metallic aluminum are bauxite, a hydrated oxide of aluminum, and cryolite, a fluoride of sodium and aluminum.

476. Preparation. — The native material from which aluminum is obtained is impure bauxite containing 50% to 75% of aluminum oxide, the remainder being chiefly silica, ferric oxide, and water. Since no satisfactory method for the purification of aluminum has been developed, the chemical purity of the compound from which aluminum is to be obtained is a matter of great practical importance. Pure aluminum oxide prepared from bauxite is the material employed.

The process used for the extraction of aluminum is the electrolysis of pure aluminum oxide dissolved in a suitable solvent. The solvents used for aluminum oxide consist of melted mixtures of the fluorides of sodium, aluminum, and sometimes calcium. The heat generated during the passing

of the electric current keeps the furnace charge melted. During the electrolysis, only the aluminum oxide is decomposed.

The apparatus used (Fig. 196) consists of a rectangular box lined with a thick layer of carbon which constitutes the cathode. Carbon rods placed in rows serve as anodes. These are arranged so that they can be lowered into the bath.

When the current passes, aluminum from the dissolved aluminum oxide passes to the cathode and collects on the

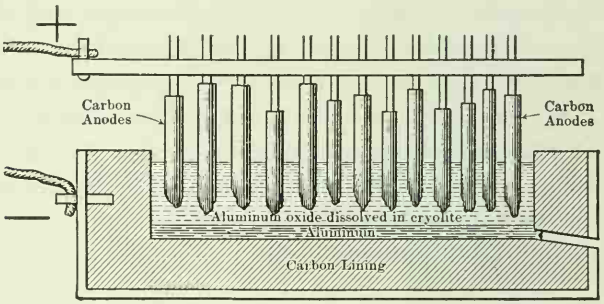


FIGURE 196.

When the current passes through the solution of aluminum oxide in melted fluorides, aluminum gathers at the bottom, while oxygen is liberated at the anode rods. These are slowly consumed by the action of the oxygen.

bottom of the box. The electrolytic cell is tapped from time to time and the liquid aluminum is run off into molds. The oxygen of the aluminum oxide is liberated at the anodes. There carbon monoxide is formed, which burns to carbon dioxide as soon as it reaches the air.

Dry aluminum oxide is stirred into the bath from time to time to replace that decomposed during the electrolysis.

477. Physical Properties. — Aluminum is a silver white metal, capable of a high polish. The dull surface usually

seen is the result of a thin coating of the oxide. Aluminum is lighter than any other of the common metals, having about the same density as glass and about one third that of copper. It is malleable and ductile, but is only half as tenacious as copper. It ranks next to silver, copper, and gold in thermal and electrical conductivity.

478. Chemical Properties. — Pure aluminum is practically unaltered in air. When aluminum powder or foil is strongly heated, it burns with a very brilliant light, resembling that of burning magnesium, and liberates a great deal of heat.

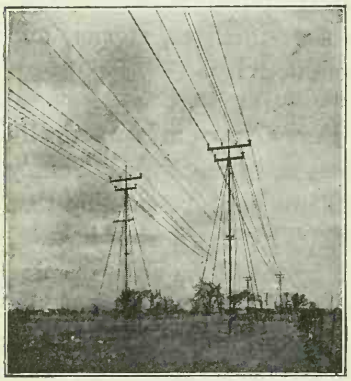
Aluminum reacts readily with hydrochloric acid, forming aluminum chloride. Aluminum is scarcely affected by nitric acid at any temperature. Dilute sulphuric acid acts very slowly with aluminum, with the liberation of hydrogen. With the concentrated acid it behaves somewhat like copper, liberating sulphur dioxide. Aluminum is also dissolved by sodium and potassium hydroxides, with the formation of the corresponding aluminates and the liberation of hydrogen:

$$2\,Al + 6\,NaOH \longrightarrow 2\,Na_3AlO_3 + 3\,H_2\uparrow$$

479. Uses. — Aluminum cooking utensils, when made of the pure metal, prove very satisfactory, because it is an excellent conductor of heat, is not attacked by common foods, and does not corrode in air. Many small useful and ornamental articles are made of it. Powdered aluminum is extensively used as a paint to protect other metals from corrosion, and in flash powders for photography. Aluminum is difficult to solder, so the parts of the larger articles are commonly welded together.

Aluminum is being used to a considerable extent in place of copper as an electric conductor for transmission lines (Fig.

197). An aluminum wire, having the same conducting power as copper, weighs one half as much and so does not produce so great a strain on the supports. Aluminum is not used for insulated wire because the increased size offsets the advantage gained by the decreased weight.



Courtesy of the Niagara Falls Power Co.

FIGURE 197.

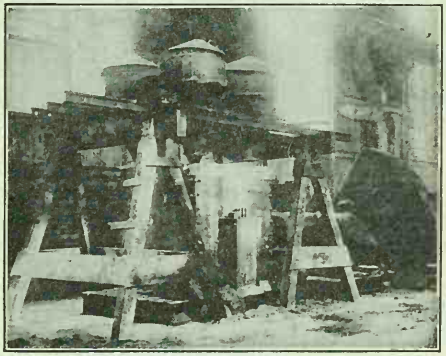
These aluminum wires convey a current that transmits 40,000 horsepower at 22,000 volts.

480. Aluminum Alloys.— Aluminum forms alloys with many of the metals. The most important are its alloys with copper in varying proportions, of which *aluminum bronze* is the most valuable. This is hard, elastic, unaltered in air, easily cut, and has a color resembling gold. It has been successfully used in place of steel for small objects, such as watch springs and ball bearings.

The addition of a small percentage of copper and zinc in casting aluminum greatly increases the strength of the casting, without changing appreciably the chemical and physical properties of the resulting metal. Most aluminum castings are alloys of copper and aluminum. *Magnalium* is the trade name for an alloy of aluminum with magnesium and other metals. The metals used with aluminum and their proportions vary according to the use to be made of the alloy. It always contains 90% aluminum and less than 2% magnesium. The tensile strength of magnalium is much higher than that of aluminum, and it can be turned in a lathe.

It is less corroded by air than aluminum, copper, zinc, or brass.

In casting other metals, the addition of a small percentage of aluminum greatly improves the texture and tensile strength of the casting; in a similar way, small quantities of other metals greatly increase the tensile strength of aluminum and make it easier to work in the shop, provided the alloying be skillfully done. A slight variation of the melting temperature seems to cause a great difference in the product.



Courtesy of the Metal and Thermit Corporation.

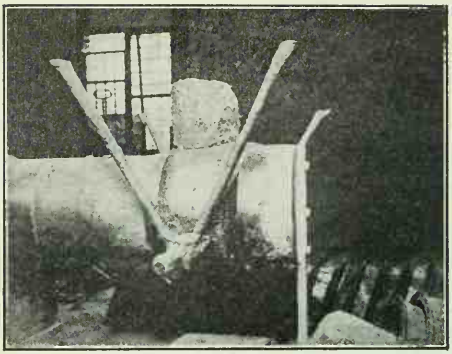
FIGURE 198.

A broken crank-shaft of a huge engine is being repaired. The four conical shaped vessels contain iron oxide mixed with aluminum, which, when the reaction starts, acts as a reducing agent and sets free iron heated far above its melting point by the energy of the reaction.

481. Thermit Process. — Aluminum is a very powerful reducing agent. Owing to this fact, we have a convenient means of obtaining metals such as chromium and manganese in the free state. When a mixture of aluminum powder and an oxide of the metal is ignited, a rapid combustion and a very high temperature result:

$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr$$

The *thermit process*, a very valuable method for repairing heavy iron machinery, and for welding together the ends of



Courtesy of the Metal and Thermit Corporation.

FIGURE 199.

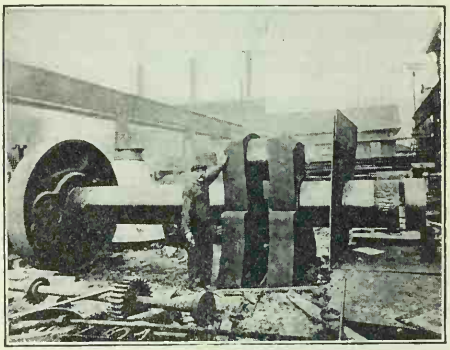
The break has been repaired. The next step is to trim away the metal which filled channels left in the molds for the escape of gases.

rails or beams, is based on the same principle. Its value in this case is chiefly due to the high temperature (3000°) produced in the reduction of iron oxide by aluminum:

$$Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3$$

This reduction takes place in a conical shaped vessel, from which the intensely hot iron flows into the crevice between the two pieces of iron to be joined (Figs. 198, 199, 200).

482. Aluminum Oxide. — The occurrence of this compound, Al_2O_3, as corundum and emery, has already been mentioned. It is easily formed as a white, amorphous powder by igniting the hydroxide. Synthetic rubies, sapphires, and other



Courtesy of the Metal and Thermit Corporation.

FIGURE 200.

The thermit operation has been completed and the broken crank-shaft is as strong as ever.

gems can be artificially prepared by fusing aluminum oxide mixed with small quantities of compounds to give the desired color; potassium dichromate gives the ruby color, and a trace of titanium oxide produces the sapphire blue.

Emery, aluminum oxide mixed with various minerals, on account of its great hardness, is extensively employed as an abrasive for grinding and polishing. An artificial corundum, made by fusing bauxite in an electric furnace, makes a better abrasive than the natural emery and is manufactured and sold under the name of *alundum*.

483. Double Salts. — If potassium sulphate and aluminum sulphate are mixed in water solution in the proportion of their molecular weights, a new substance having a very characteristic crystalline form and all the characteristics of a chemical compound is formed. This is the well-known substance, *alum*, $KAl(SO_4)_2 \cdot 12\ H_2O$ (Fig. 201). It belongs to a class of substances known as *double salts*. Such salts contain two metals joined to one kind of acid radical, or one metal joined to two acid radicals.

FIGURE 201.
A mass of alum crystals, $KAl(SO_4)_2 \cdot 12\ H_2O$.

484. Alums. — This class name is given to a series of double salts which have the same crystalline form as ordinary alum, similar chemical properties, and analogous formulas. They always contain a univalent metal and a trivalent metal. *Chrome alum* has the formula $KCr(SO_4)_2 \cdot 12\ H_2O$ (Fig. 202); ammonium alum, $NH_4Al(SO_4)_2 \cdot 12\ H_2O$. The alums are

much more soluble in hot than in cold water, and are deposited from a cooling solution in well-marked crystals, usually octahedral or cubical in form.

FIGURE 202.
A crystal of chrome alum.

Ordinary alum is used for a *styptic* to check the flow of blood, and in the preparation of aluminum hydroxide for use in mordanting cloth and in clarifying water. Aluminum sulphate has largely replaced the alums industrially.

ALUMINUM HYDROXIDE

485. Preparation. — This is prepared by the addition of ammonium hydroxide to a solution of an aluminum compound. For example:

$$Al_2(SO_4)_3 + 6\ NH_4OH \longrightarrow 2\ Al(OH)_3 \downarrow + 3\ (NH_4)_2SO_4$$

Calcium hydroxide may also be used. If sodium or potassium hydroxide is employed, it reacts in excess with aluminum hydroxide, forming an aluminate and water:

$$3\ KOH + Al(OH)_3 \longrightarrow K_3AlO_3 + 3\ H_2O$$

Aluminum hydroxide is an amorphous, translucent substance, insoluble in water. It reacts with acids, forming the corresponding aluminum salts; but, as we have just seen, it also reacts with strong bases in the manner of an acid. Aluminum hydroxide, $Al(OH)_3$ or H_3AlO_3, has, therefore, a double or amphoteric character, acting as an acid or as a base according to the nature of the substance with which it is reacting. This indicates that aluminum hydroxide ionizes in two different ways:

$$Al(OH)_3 \rightleftharpoons Al^{+++} + 3\ OH^-$$

$$H_3AlO_3 \rightleftharpoons 3\ H^+ + AlO_3^{---}$$

On being heated, aluminum hydroxide is converted into aluminum oxide:

$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O$$

486. Mordants and Lakes. — The amorphous character of the hydroxide renders it valuable in dyeing and water purification. Many dyestuffs do not readily enter the fiber of cotton goods, so it is necessary to use some substance to cause the dye to adhere and prevent it from washing off. Such a substance is called a *mordant.* It is found that when aluminum hydroxide is precipitated in a solution containing coloring matter, the color is carried down by the colloidal hydroxide as it settles, leaving the solution clear. The combination of the color and aluminum hydroxide is called a *lake;* lakes are used in dyeing and as pigments. In dyeing cotton, aluminum hydroxide is sometimes precipitated on the fiber, either by soaking the cloth first in alum and then in ammonium hydroxide solution, or by impregnating it with aluminum acetate, which yields the hydroxide on heating. The cloth, mordanted with aluminum hydroxide, is soaked in the dye, which forms an insoluble lake with the mordant, and thus produces a fast color. Other amorphous hydroxides, as those of iron and copper, are also used as mordants.

Many mordants react chemically with the dye, producing new shades. So it is possible, by the use of the proper mordants, to secure different colors from the same dye. This is done in one method of calico printing, where the pattern is first stamped with a mordant. When the cloth is passed

through the dye, the mordanted portions take it up and retain it, while the color is removed from the unmordanted parts by washing.

487. Coagulum in Water Purification. — The use of aluminum hydroxide in water purification is similar to that in dyeing; it carries down with it suspended particles of foreign matter (Fig. 203). Colloidal action (§ 358) has a

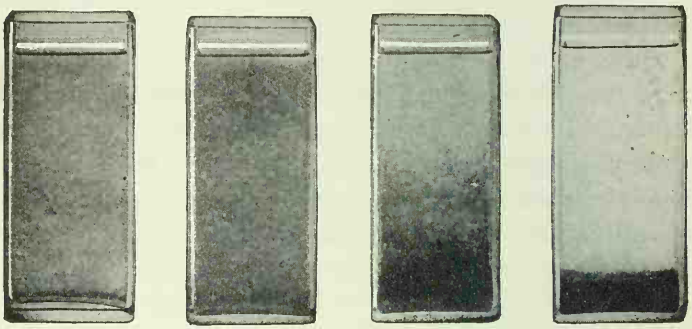


FIGURE 203.

These jars show how aluminum hydroxide clarifies muddy water. In the first jar the precipitate has just been formed. The other jars show, in successive stages, how the precipitates entangle the muddy particles and carry them down in the settling process.

good deal to do with the purification of water by the use of aluminum hydroxide. Bacteria are largely colloidal and are coagulated and killed by the H^+ ions that result from the hydrolysis of the alum that is used to form the aluminum hydroxides. Aluminum hydroxide as a colloid is positively charged. Hence the latter attracts and absorbs the bacteria. Colloidal clay is negatively charged and is attracted to aluminum hydroxide in a similar way. Coloring matter, if present in water, is positively charged and is attracted and

coagulated by the negative charge of the sulphate ions that are furnished by the alum, which is used to make the precipitate of aluminum hydroxide.

The hydroxide is produced in this case by adding proper proportions of aluminum sulphate and lime:

$$3\ Ca(OH)_2 + Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3\downarrow + 3\ CaSO_4$$

The aluminum hydroxide is completely removed by precipitation; the precipitate carries with it the greater part of the sediment and disease germs. The calcium sulphate is partly precipitated and partly dissolved, adding to the hardness of the water. In water containing a considerable amount of calcium, magnesium, or ferrous bicarbonates in solution, these salts are sufficient to precipitate the hydroxide. In such cases, aluminum sulphate or alum is added to the water and the precipitation takes place without lime:

$$3\ Ca(HCO_3)_2 + 2\ Al_2(SO_4)_3 + 6\ H_2O \longrightarrow 3\ CaSO_4 + 3\ H_2SO_4 + 4\ Al(OH)_3\downarrow + 6\ CO_2\uparrow$$

$$3\ Ca(HCO_3)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4 + 6\ H_2O + 6\ CO_2\uparrow$$

Aluminum Silicates

488. Clay and Pottery. — Ordinary clay is an impure silicate of aluminum; *kaolin* is a pure form of a similar deposit. Both are formed by the decomposition of feldspar rock. Feldspar is a double silicate of aluminum and an alkali metal. When it is exposed to the action of the weather, the alkali silicate is removed by the water and carbon dioxide, and the residue left is *kaolin*, or clay containing other rock materials, as sand and mica. Pure kaolin is a white, pulverulent mass; when wet, it is plastic and can be molded.

When the molded clay is heated and dried, it shrinks. Iron compounds often give clay a red color, seen in some bricks, and in roofing and drain tiles. Light brick is made from clay containing little or no iron. Clay containing silica is used for fire-bricks, stove linings, and crucibles.

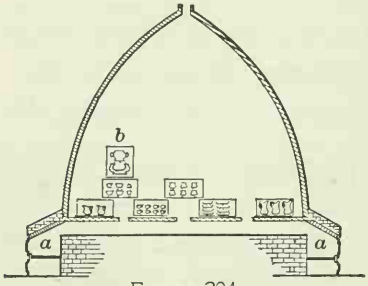


FIGURE 204.

A diagram of a china kiln, showing the fire-boxes (*a*) and the saggars (*b*) containing different articles of porcelain ware.

Bricks, earthenware, porcelain, and china are made by molding the clay or kaolin into the desired form and baking in a furnace or *kiln* (Fig. 204). In making common earthenware articles, the baking temperature is not very high, and the mass being porous, as in flower pots, will not hold water. In making roofing tiles, jugs, and drainpipes, salt is thrown into the fire; it volatilizes and forms on the surface of the articles a *glaze* impervious to water, consisting of a fusible silicate of sodium and aluminum.

Stoneware and crockery are made from purer varieties of clay, and are more carefully molded.

Copyright by Keystone View Co.

FIGURE 205.

Clay is shaped on the potter's wheel into vases of beautiful form.

In addition to the clay, they contain some fusible, hardening material. A heavier and more durable glaze is used than that on earthenware.

489. Porcelain and china are made from pure kaolin, feldspar, and quartz. The materials are ground fine, thoroughly mixed, and wet. The wet mass is then modeled on a potter's wheel (Fig. 205) or molded in plaster of Paris molds and dried; when dry enough to handle, the mold is removed and the article smoothed. It is then *fired* at a low temperature which leaves it firm and hard, but porous and ready for the glaze. This consists of feldspar and quartz ground fine and suspended in water. The article is dipped into the mixture and dried. It is then placed in a *saggar* or fire-clay box (Fig. 204, *b*) and supported on a tripod in such a way that it shall not touch the box. This is placed in the kiln, the temperature of which is gradually raised to a red heat, an operation requiring from twelve to twenty-four hours. The temperature is then increased for three days or more, and finally allowed to fall very slowly. The mass is now hard, dense, white, translucent, thin, and not easily affected by chemicals, except alkalies. The colors that are

Copyright by Underwood and Underwood.

FIGURE 206.

The unbaked pottery is about to be put into the kiln.

used in decorating china are composed of substances that are stable at the high temperature necessary for the fusion of the glaze.

490. Cement and Concrete. — Hydraulic cement results from the heating of a mixture of limestone (calcium carbonate) and clay (aluminum silicate) until they just begin to melt together (Fig. 207). Many natural limestones contain

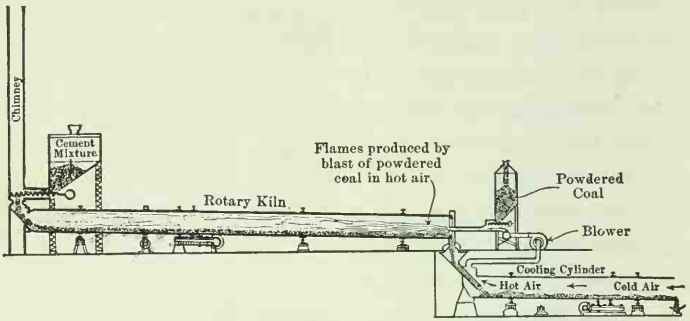


FIGURE 207.

A kiln in which cement is made. Note how the air used to burn the fuel is preheated with heat that would otherwise be wasted.

the aluminum silicate mixed with the calcium carbonate in nearly the required proportions. Such cement rocks, when burned in a manner similar to that used in making quicklime (§ 381), yield *natural cements*. Artificial cements are made by "burning" clay or shale with marl, limestone, or chalk.

The rock materials are crushed in the proportion of about 1 part of silicate to 3 parts of carbonate, and finely powdered. After thorough drying, the mixture is burned in long, inclined, rotary kilns, through which it passes from the comparatively cool upper part to the intensely heated lower end.

The lumps of the semi-fused material that issue are cooled and ground to an extremely fine powder. The quality of the cement depends to an important degree on the fineness of the grinding.

491. Setting of Cement. — Cement is believed to consist of a mixture of calcium silicate and calcium aluminate. When it is mixed with water and the mass allowed to stand, it solidifies or "sets." The reaction that takes place is probably a conversion of the calcium and aluminum silicates of the dry cement into other colloidal silicates of the same metals containing combined water (§ 360). Calcium hydroxide is probably also set free during this reaction and hardens as it does in the parts of mortar that are not exposed to the air (§ 386). As the constituents of the air have no part in the setting of cement, it goes on as well under water as in the air, and inside of the mass as well as on the outside. The increase in hardness and strength goes on rather rapidly during the first few days after the cement is mixed with water, and then more slowly, but the cement continues to gain strength for years.

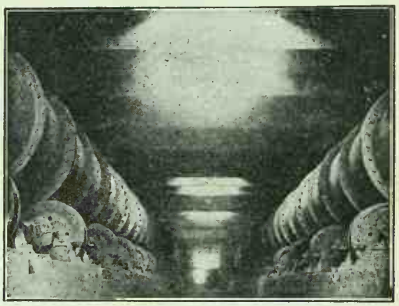


FIGURE 208.
Looking down the passage between two cement kilns. The rotating cylinders are 100 feet long.

492. Concrete; Reënforced Concrete. — The chief use of cement is in making concrete, a mixture of sand and broken

stone or gravel with cement and water. Concrete is used for the foundations, floors, and walls of buildings, by pouring the wet concrete into forms made of board or steel. After it is thoroughly set, it gives a mass that has enormous strength in resisting pressure. This strength may rise as high as 7000 pounds to the square inch. But concrete is not so resistant against *tensional* (pulling) stresses. To meet this need, twisted steel rods are set in the molds in such a way that they become surrounded by and enveloped in the concrete (Fig. 209). Such structural work is known as *reënforced concrete*. Its use has revolutionized building processes in the last few years.

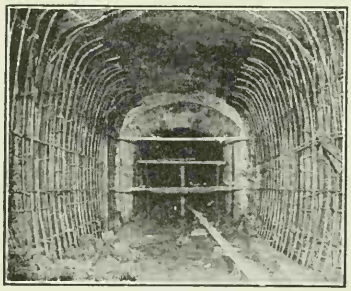


FIGURE 209.

Showing how iron rods are placed in making a reënforced concrete lining for a New York subway.

Concrete is indispensable for bridge piers and other work below water.

SUMMARY

Aluminum does not occur native. Its oxides and silicates are found widely distributed.

It is **prepared** by the electrolysis of oxide of aluminum dissolved in a melted mixture of fluorides.

Aluminum is a silver-white metal; specific gravity 2.6; melting point 657°. It is a good conductor of heat and electricity.

Aluminum **dissolves** in hydrochloric acid and in sodium hydroxide solution. Hydrogen is evolved.

It is **used** for cooking utensils, flashlight powders, foil, ornamental

articles, cables for conducting electricity, aluminum bronze, and other alloys.

Corundum, ruby, and sapphire are nearly pure **aluminum oxide.** Emery is corundum mixed with iron oxide.

Potash **alum** has the formula $KAl(SO_4)_2 \cdot 12\ H_2O$. Other alums have the same crystalline form and analogous formulas. They always contain a univalent metal (or radical) and a trivalent metal.

Aluminum hydroxide possesses the properties of a base and those of an acid.

It is used as a mordant and in the purification of water.

Clay is an impure silicate of aluminum and is used in the manufacture of bricks and of earthenware.

Kaolin, nearly pure aluminum silicate, is used in the manufacture of porcelain and of china.

Cement is made by heating to incipient fusion a mixture of limestone and clay, and grinding the mixture fine. Cement hardens under water.

Concrete is a mixture of sand and gravel, or broken stone, with cement and water.

Reënforced concrete is concrete in which steel rods are embedded to take up the tensional stresses.

EXERCISES

1. Why should not a solution of sodium hydroxide be concentrated in an aluminum dish?

2. Would you carry on the electrolysis of sodium chloride in an aluminum dish? Explain.

3. Name three advantages in the use of aluminum for kitchen utensils.

4. For what purposes is aluminum bronze used?

5. What would be the weight of a piece of aluminum containing a cubic foot? A cubic foot of water weighs 62.5 pounds.

6. How much aluminum is contained in 200 tons of aluminum oxide?

7. Describe how the broken propeller shaft of an ocean steamer could be repaired by thermit. Show the economy of the process.

8. Write formulas for the following alums: sodium chromium alum, ammonium iron alum, potassium iron alum.

9. How much calcium hydroxide would be required to combine with 20 kilos of aluminum sulphate?

10. Compare the action of aluminum sulphate and copper sulphate in water purification.

11. Write an equation showing how aluminum hydroxide can play the part of a base; of an acid.

12. What compound of aluminum is formed when a solution of calcium bicarbonate reacts with a solution of aluminum sulphate?

13. What is a mordant? A lake?

14. What is meant by saying that aluminum hydroxide has an amorphous character? An amphoteric character?

15. What advantage has concrete in building foundations for bridge piers and dams?

16. Explain why steel rods are used in reënforced concrete.

17. Compare the hardening of cement with that of mortar.

18. How many liters of hydrogen would be liberated by the addition of 9 grams of aluminum to an excess of hydrochloric acid?

19. Describe briefly or define: alum, concrete, porcelain, emery, aluminum bronze.

CHAPTER XXXV

TIN AND LEAD

Tin was one of the earliest metals known. The Phœnicians obtained it from the British Isles, which they called Cassiterides, land of tin. As a constituent of bronze it was used before iron.

493. Metallurgy of Tin. — Tin oxide, SnO_2, is the only available ore. The present commercial supply comes principally from Bolivia and the Malay States. Tin oxide is reduced by heating it in a reverberatory furnace with coal:

$$SnO_2 + C \longrightarrow Sn + CO_2 \uparrow$$

The molten metal, which collects at the bottom of the furnace, is drawn off and cast into ingots, known commercially as *block tin*. Tin is refined by electrolysis.

494. Properties of Tin. — Tin is a white, lustrous metal, capable of withstanding the ordinary atmospheric agents. Being soft and malleable, it can be cut and hammered. Like zinc, it is crystalline in structure, and if a bar of tin is bent, it makes a peculiar noise (*tin cry*), probably caused by the friction of the crystals. Like zinc, its physical properties vary considerably with the temperature. It melts at a rather low temperature, 232° C., and burns, forming a white oxide.

With acids tin does not react like any *one* of the other

metals; with hot, concentrated hydrochloric acid, it forms *stannous chloride*, $SnCl_2$; with sulphuric acid it reacts like copper; nitric acid oxidizes it to a white, insoluble solid known as metastannic acid.

Tin can be separated from solutions of its compounds as a gray, spongy mass, by immersing a strip of zinc in the solution (Fig. 210):

$$Sn^{++} + 2\,Cl^- + Zn \longrightarrow Sn\downarrow + Zn^{++} + 2\,Cl^-$$

495. Electrochemical Series. — This reaction is analogous to the reduction of a silver salt by copper. Zinc immersed in a solution of tin, lead, copper, silver, or gold will become ionized and dissolve, and then the metal previously dissolved, losing its charge, will separate from the solution.

In a similar manner lead will reduce the metallic ions of copper, of silver or of gold in solutions of their salts. Copper will replace silver or gold and silver will replace gold.

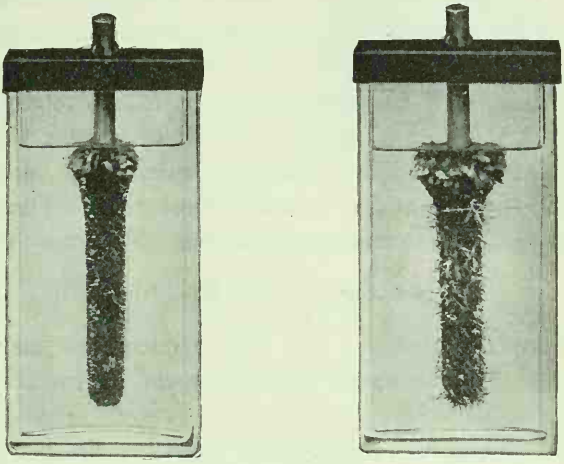
The electrochemical series of the elements is an arrangement in such an order that each will replace those below it in the list.

The metals at the top of the list are the more reactive, they corrode easily, and are more difficult to obtain. They never occur free in nature. Those at the bottom often occur free in nature, or are easily reduced, and do not ordinarily corrode.

Electrochemical Series
Potassium
Sodium
Magnesium
Aluminum
Zinc
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Arsenic
Mercury
Silver
Platinum
Gold

496. Uses of Tin. — The available supply of tin is not large. It is not a cheap metal, so that objects of pure tin are

not in common use. The resistance of tin to ordinary corrosive agents is utilized in protecting other metals by covering them with a layer of tin. Ordinary *tinware* is sheet iron, which has been thoroughly cleaned and dipped



a *b*

FIGURE 210.

Zinc replaces tin in a solution of stannous chloride. *a* shows the result five minutes after the zinc rod has been placed in the solution; *b* shows the needle-like crystals of tin that develop within twenty minutes.

into melted tin. Copper vessels and brass pins are similarly treated.

Tin foil is tin, hammered or rolled into thin sheets; cheaper grades contain some lead. Pipes made of pure tin (*block tin*) are used in water stills and to convey soda water from the tanks to the faucet.

Many common alloys contain tin. Bronze contains copper, tin, and often zinc. The one cent piece is bronze. Pewter and solder contain tin and lead. Britannia metal and

white metal contain varying proportions of tin, antimony, and copper. Anti-friction and fusible metals often contain considerable tin.

497. Compounds of Tin. — *Stannous chloride*, formed by the reaction of tin and hydrochloric acid, is the only common compound. The hydrated salt, $SnCl_2 \cdot 2\,H_2O$ is technically known as *tin crystals*, and is extensively used in mordanting. It produces more brilliant shades than the aluminum compounds. Stannous chloride is a strong reducing agent in acid or in alkaline solutions. Ferric salts are reduced by it to ferrous compounds:

$$2\,FeCl_3 + SnCl_2 \longrightarrow 2\,FeCl_2 + SnCl_4$$

Mercuric compounds are first reduced to mercurous salts, and with an excess of the reagent, to metallic mercury:

$$2\,HgCl_2 + SnCl_2 \longrightarrow 2\,HgCl\downarrow + SnCl_4$$
$$2\,HgCl + SnCl_2 \longrightarrow 2\,Hg\downarrow + SnCl_4$$

The *stannic chloride*, $SnCl_4$, is a colorless, fuming liquid. This, like other tin salts, is readily hydrolyzed by water.

Thus the valence of tin may be two or four, as shown by the existence of the stannous and the stannic compounds. *Stannous sulphide*, SnS, is a brown, insoluble compound. *Stannic sulphide*, SnS_2, is a yellow, insoluble solid used as a pigment.

Lead

Owing to the wide distribution of its compounds and the ease of separation from its ores, lead has been used by man from the earliest times.

498. Metallurgy. — The most common ore is the sulphide, galena, PbS (Fig. 211), large deposits of which are found in Missouri, Illinois, and Colorado. The method employed in the extraction depends largely upon the purity of the ore.

FIGURE 211.
Crystals of the mineral galena, lead sulphide.

Ores having a large percentage of lead are roasted in a reverberatory furnace (Fig. 212) until two thirds of the sulphide has been oxidized, forming lead oxide and sulphur dioxide.

$$2\ PbS + 3\ O_2 \longrightarrow 2\ PbO + 2\ SO_2\uparrow$$

When the oxidation has proceeded far enough, the air is shut off by closing the doors, and the mixture is heated to a higher temperature. The remaining lead sulphide now reacts with the lead oxide, forming lead and sulphur dioxide:

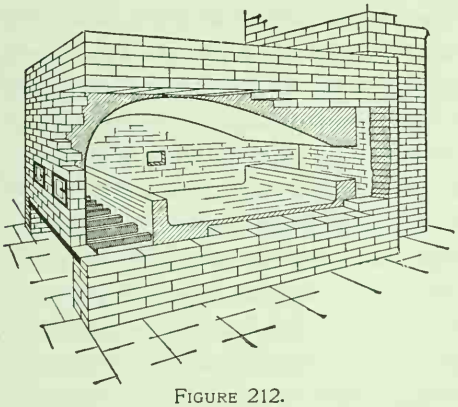


FIGURE 212.
A diagram of a reverberatory furnace. Flames from the fuel do not touch the melted metal, but their heat is reflected downwards from the heavy, arched brick roof.

$$PbS + 2\ PbO \longrightarrow 3\ Pb + SO_2\uparrow$$

The sulphur dioxide passes off as a gas. The lead is molded into ingots known as *pig lead.*

When there is a considerable amount of precious metal in the lead, it is known as *base bullion.* The working of this has already been described under silver (§ 455, Parkes' process).

Ores poor in lead are reduced in a blast-furnace similar to that used for copper; indeed, they may be separated from the ore at the same operation, the heavy lead settling beneath the matte and slag.

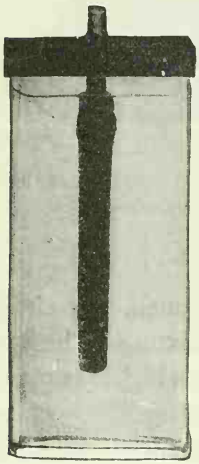


FIGURE 213.

A rod of zinc has been placed in a solution of lead nitrate. As the zinc passes into solution, crystals of lead begin to adhere to the rod.

499. Properties of Lead. — Lead is the heaviest of the common metals. It is soft and bluish white. The brilliant luster, apparent when freshly cut, soon disappears, owing to the formation of a thin film of oxide. This coating, however, protects it from further change. Lead is not very tenacious, but being soft it can be rolled into sheets or forced through a die to form pipe.

When heated in air, lead oxidizes. Neither cold hydrochloric nor sulphuric acid has much effect on it. Nitric acid, acetic acid (from vinegar), and many vegetable acids dissolve it, forming soluble salts. Water containing carbon dioxide corrodes lead, hence the objection to lead water-pipes, since the water by this action might carry away poisonous lead compounds in solution.

All lead compounds are poisonous, and if taken into the system cause serious illness. Even minute quantities in the water will ultimately produce this result, for lead

compounds are excreted with difficulty, and therefore accumulate in the body. Painter's colic is a form of chronic lead poisoning.

On immersing a strip of zinc in a solution of a lead salt, the lead separates in a characteristic crystalline deposit, the *lead-tree* (Fig. 213):

$$Pb^{++} + 2\ NO_3^- + Zn \longrightarrow Zn^{++} + 2\ NO_3^- + Pb\downarrow$$

The formation of insoluble chrome yellow by addition of potassium chromate to a solution of a lead salt is another characteristic property of lead salts:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2\ KNO_3$$

500. Uses of Lead. — Lead is cheap, is easily worked, and is durable, so that it is one of our most common and most valuable metals. Its density is sometimes an advantage. Lead is very extensively used for pipes and as a sheathing for cables, as it is easily cut, bent, or soldered. Lead pipe is now made by forcing the hot lead through a die by means of the piston of a hydraulic press. The opening of the die is partly obstructed by a solid cylindrical rod attached to the upper surface of the piston. This rod moves upward with the piston, and the pipe is formed by the lead being squeezed out between the rod and the wall of the die.

As it withstands ordinary atmospheric conditions, sheet lead was formerly used for roof covering. It is very widely used as a lining for tanks, cisterns, and cells used in electrolytic operations. The Chinese have long used it for lining tea chests. Thin sheet lead, alloyed with tin, is often used instead of pure tin foil for protective coverings.

Alloys of lead are numerous and in general are durable and easily worked. *Type metal* contains lead, with tin and

antimony which harden it. The alloy melts easily and expands on solidifying. Thus it fills the molds and makes a clear-cut type. *Solder* and fusible metals are largely lead and tin. Such easily melting alloys are forced through a die in the same manner as lead pipe, forming a wire used as *fuse wire.*

Large quantities of lead are used in the manufacture of *shot.* As already stated, the shot contains a small amount of arsenic. The molten metal is run into a perforated vessel, and falls in streams from a considerable height into the water. In falling, the streams separate into drops, which solidify before they reach the water. The sizes of shot are assorted by allowing them to run down inclined planes and over screens of different meshes. The smallest shot fall through the nearest (smallest) openings into the bins, the larger shot going on to the larger holes. Irregular shaped pieces will not roll well, and are finally pushed off at the end. The shot are polished by tumbling them in a barrel or drum with a little graphite.

Compounds of Lead

501. Oxides.—*Lead monoxide,* PbO, when of a yellowish tint, is known as *massicot;* when it solidifies from the molten state it is buff-colored and crystalline, and is known as *litharge.* The presence of bismuth sometimes gives the litharge a yellowish color. Litharge is made by heating lead in the air. Considerable quantities of lead oxide are produced in the cupellation of silver. It is largely used in the preparation of oils and varnishes, of glass and glazes, and in making other compounds of lead. A mixture of litharge and glycerine is used as a cement, especially for stone and glass.

Red lead, or minium, is a bright red powder, known as American vermilion. It is prepared by heating lead or lead oxide in the air, oxygen being absorbed in the operation. The tint and composition often vary with the manipulation. Its composition may be represented by the formula: Pb_3O_4 or $2\,PbO \cdot PbO_2$. It is used in making flint glass and as a pigment, especially on ironwork. Being an oxidizing agent, it hastens the hardening of the oils used in paint. On this account a mixture of red lead and oil is used by plumbers and gas fitters to make tight joints.

Lead dioxide, PbO_2, also called lead peroxide, is a brown powder obtained by treating red lead with nitric acid. It is used as an oxidizing agent on the positive plates of storage batteries.

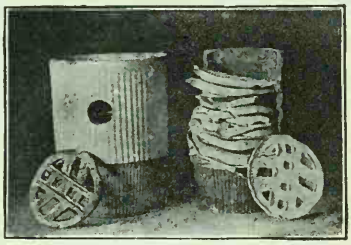


FIGURE 214.

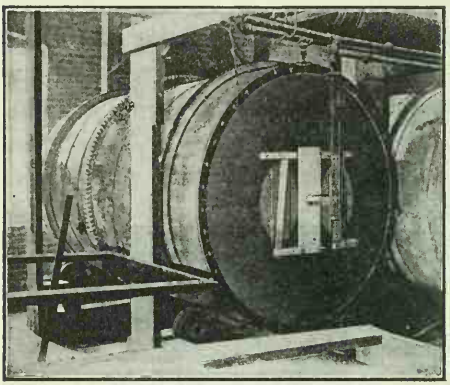
The jars and lead buckles used in the old Dutch process of making white lead. A little acetic acid is put into each jar, and the carbon dioxide is produced by the fermentation of tan bark in which the jars are packed.

502. White Lead, or *basic lead carbonate*, is a heavy, white, opaque powder. It mixes well with linseed oil and forms a valuable paint base. The basis of many paints is white lead, which furnishes opacity or *body*, different colors being produced by the addition of color materials or pigments.

Owing to the importance of white lead, many methods have been devised for its production.

The *Dutch process of corrosion* has been in use three hundred years, and although details have been improved, remains essentially the same. Ridged and perforated

disks, or "buckles," of lead (Fig. 214) are piled in a loosely covered earthenware pot, the lower part of which contains a little dilute acetic acid. Such pots are placed side by side and covered with moist tan bark; other layers of pots are added to a considerable height. The decaying organic matter generates carbon dioxide and heat. The acetic acid is volatilized by the heat and reacts with the lead, forming basic lead acetate. The carbon dioxide resulting from the fermentation changes this to the basic carbonate. Three or four months are required for the complete corrosion of the lead; the right-hand portion of Figure 214 represents a jar broken open to show the lead buckles after corrosion. The white lead is removed from the jars, and small pieces of unaltered lead are removed by screening. It is then ground wet, washed, strained through fine silk sieves, and allowed to settle. The white lead is finally ground in oil and is ready for use. The corrosion process requires much time but yields good paint. The Dutch process aims at a white lead with the composition $Pb(OH)_2 \cdot 2\ PbCO_3$, but the composition of the product varies.



Courtesy of the Carter White Lead Co.

FIGURE 215.

Finely divided lead is produced by blowing steam through the melted metal. In this rotating drum the lead is exposed to the action of dilute acid and carbon dioxide.

A much quicker corrosion is obtained by blowing the melted lead into a fine spray by a blast of steam, and treating the resulting powder with a stream of carbon dioxide in the presence of moist air and acid, in a rotating cylinder (Fig. 215).

The commercial white paints are generally mixtures of white lead and zinc white. Calcium carbonate, barium sulphate, silica, and other substances are frequently used as extenders, that is, these materials make the more expensive white lead spread over a greater surface.

503. Chrome Yellow. — *Lead chromate,* $PbCrO_4$, is an insoluble, bright yellow powder, prepared by mixing solutions of lead salts and chromates. It is used in dyeing and painting.

SUMMARY

The chief ore of **tin** is the oxide, which is reduced by heating with coal.

Tin is soft, malleable, and crystalline. Its specific gravity is 7.3, and it melts at 232° C.

It is **unaltered by air.**

Tin is **used** for pipe, as foil, and as a coating for iron. It is a constituent of bronze, pewter, and white metal.

Stannous chloride is formed by the action of hydrochloric acid on tin. It is a reducing agent.

Lead occurs chiefly as a sulphide. The ore is reduced in a reverberatory furnace.

Lead is soft, malleable, and tenacious. Its specific gravity is about 11.3 and its melting point 327° C.

It oxidizes in air and dissolves in nitric and acetic acids. Water containing carbon dioxide corrodes it, producing poisonous compounds.

Lead is **used** for pipe, as a lining, a covering material, and in alloys, such as type metal, solder, and shot.

Lead oxides are made by heating lead in air. They are used in making varnishes and glass, and as pigments. Lead dioxide is used in storage batteries.

White lead is basic lead carbonate. Chrome yellow is lead chromate.

EXERCISES

1. Which forms the better protective coating for iron, — tin or zinc? Why?

2. Name uses in which the weight of lead is an advantage.

3. Why were lead and tin early obtained in the metallic state?

4. Why is tin foil superior to lead foil for wrapping articles of food?

5. Why is arsenic put in shot?

6. What is litharge? Red lead? White lead?

7. Why is red lead called a drier in paints and varnishes?

8. What advantage has zinc white over white lead as a paint base? White lead over zinc white?

9. What are the characteristic properties of glass containing lead?

10. How much lead can be extracted from a ton of galena?

11. In converting a ton of lead oxide (PbO) into red lead (Pb_3O_4), how much oxygen is absorbed?

CHAPTER XXXVI

MANGANESE, CHROMIUM, COBALT, AND NICKEL

Manganese

504. Preparation and Properties. — The most important ore of manganese is pyrolusite, which is crude manganese dioxide. The metal is obtained by igniting a mixture of pyrolusite and aluminum powder. Heat is applied at one point and the action spreads through the whole mass:

$$3\,MnO_2 + 4\,Al \longrightarrow 2\,Al_2O_3 + 3\,Mn$$

Manganese is a hard metal resembling steel in appearance. It oxidizes in moist air and, when finely divided, decomposes boiling water. It dissolves readily in sulphuric and hydrochloric acids, with the liberation of hydrogen and the formation of the corresponding salt of the manganous ion, Mn^{++}:

$$Mn + 2\,H^+ + SO_4^{--} \longrightarrow Mn^{++} + SO_4^{--} + H_2\uparrow$$

Its iron alloys, ferromanganese and spiegeleisen, are used in the production of Bessemer iron and steel. Manganese steel is a tough, tenacious steel.

505. Manganese Compounds. — Manganese forms several oxides, of which the most important is the *dioxide*, MnO_2. This is a hard, black solid which conducts electricity. It is a powerful oxidizing agent, as we have already seen in

the preparation of chlorine from hydrochloric acid (§ 86). Its conducting power and oxidizing action make it a valuable depolarizer in voltaic cells (Fig. 216).

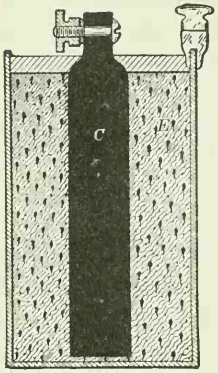


FIGURE 216.

In the dry battery, manganese dioxide serves as an agent to oxidize hydrogen which would otherwise gather on the carbon rod (*C*) and interfere with the action of the cell.

The manganous salts are stable compounds, whose water solutions are pink. The salts of the manganic ion Mn^{++++} are unstable.

506. Manganates and Permanganates. — Since manganese is one of the elements that display both metallic and non-metallic characteristics, we have salts in which it occurs as a constituent of the negative ion.

The most important of these salts are the manganates and the permanganates, both of which contain the radical MnO_4. In the manganates the ion is bivalent, MnO_4^{--}; in the permanganates it carries only one charge, MnO_4^{-}. Corresponding to this difference in valence of the ion are differences in the properties of the salts. The manganates are green and the permanganates are purple.

Potassium manganate is made by fusing a manganese compound with potassium hydroxide in the presence of air or an oxidizing agent, dissolving the residue and evaporating the solution in a vacuum. The crystals obtained are dark green. They are decomposed by water, with the liberation of manganese dioxide and the formation of potassium permanganate, $KMnO_4$:

$$3\ K_2MnO_4 + 2\ H_2O \longrightarrow 2\ KMnO_4 + MnO_2 + 4\ KOH$$

Potassium permanganate is obtained as dark purple crystals, which dissolve in water, yielding a violet solution. It is a powerful oxidizing agent, much used in analytical determinations of oxidizable materials. Since the first drop in excess of the permanganate required for the oxidation colors the solution pink, it is easy to tell when enough of the solution has been added.

Acting as an oxidizing agent in *acid* solution, 2 molecules of a permanganate yield 5 atoms of active oxygen:

$$2\ KMnO_4 \longrightarrow K_2O + 2\ MnO + 5\ O$$

The oxides of potassium and manganese that result from the breaking up of the permanganate unite with the acid present to form salts of these two elements. The five atoms of active oxygen are taken up by the oxidizable material. The full equation for the action of potassium permanganate on sodium sulphite would be:

$$5\ Na_2SO_3 + 2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow 5\ Na_2SO_4 + K_2SO_4 + 2\ MnSO_4 + 3\ H_2O$$

When acting in an *alkaline* solution as an oxidizing agent, a permanganate breaks up as follows:

$$2\ KMnO_4 \longrightarrow K_2O + 2\ MnO_2 + 3\ O$$

Chromium

Chromium occurs chiefly as chromite, $Cr_2O_3 \cdot FeO$. From this it is reduced by aluminum in a manner analogous to that employed in the preparation of manganese. It is a hard, steel-gray metal, unaltered by the air. When very small quantities are added to steel, the tenacity and hardness are increased.

507. Oxides of Chromium. — The two important oxides of chromium are *chromic oxide*, Cr_2O_3, and *chromic anhydride*, CrO_3. The chromic salts are derived from chromic oxide; the most important is the double sulphate of potassium and chromium, $KCr(SO_4)_2 \cdot 12\,H_2O$, known as *chrome alum*. A solution of chromic anhydride yields CrO_4^{--} ions, but the acid is isolated with difficulty, as it breaks up into chromic anhydride and water. The solution of the anhydride is a powerful oxidizing agent, and its derivatives, the chromates and dichromates, resemble it in this respect.

508. Chromates and Dichromates. — *Potassium dichromate*, $K_2Cr_2O_7$, is the source of most of the chromium salts. It is prepared by heating chromite with potassium carbonate and lime in a reverberatory furnace. It forms large red crystals from solution or fusion; these are somewhat soluble in cold water, and their solubility increases rapidly as the temperature rises. Potassium dichromate reacts with sulphuric acid in the presence of an oxidizable substance, with the formation of chromium sulphate and the liberation of oxygen. This oxidizing action is frequently made use of in depolarizing voltaic cells. Sodium dichromate is very similar to potassium dichromate, but has the added advantage of being more soluble. Most of the dichromates are orange in solution.

Potassium chromate, K_2CrO_4, is prepared by the addition of potassium hydroxide to the dichromate:

$$K_2Cr_2O_7 + 2\,KOH \longrightarrow 2\,K_2CrO_4 + H_2O$$

It forms yellow crystals, more soluble than those of the dichromate.

The acids from which the chromate and the dichromate are theoretically derived have the formulas H_2CrO_4 and $H_2Cr_2O_7$ respectively. *Both* of these have the anhydride CrO_3, as may be seen from the theoretical equations:

$$H_2O + CrO_3 \longrightarrow H_2CrO_4$$
$$H_2O + 2\ CrO_3 \longrightarrow H_2Cr_2O_7$$

The relation between the chromate and the dichromate is shown if the formula of potassium dichromate is written $K_2CrO_4 \cdot CrO_3$. Other complex chromates are known containing more than one CrO_3 group.

Lead chromate, $PbCrO_4$, made by treating a soluble lead salt with a chromate or dichromate, is a yellow, insoluble compound, known as chrome yellow, used as a pigment. The chromates of zinc and barium are also used as pigments.

509. Change of Valence through Oxidation. — In cases of elements which have, like manganese and chromium, a wide variety of compounds, the change of the element from one compound into another is frequently accompanied by a change of valence. We will consider the case of chromium briefly.

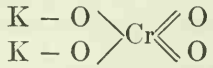
Chromous chloride, $CrCl_2$, in which the valence of the metal is 2, can be changed into chromic chloride, $CrCl_3$, where the valence is 3, by an oxidizing agent. The presence of hydrochloric acid enables us to write a simpler equation:

$$2\ CrCl_2 + 2\ HCl + O \longrightarrow 2\ CrCl_3 + H_2O$$

Chromic compounds can be converted into chromates by melting them with a base and an oxidizing agent, such as potassium chlorate:

$$2\ CrCl_3 + 10\ KOH + 3\ O \longrightarrow 2\ K_2CrO_4 + 6\ KCl + 5\ H_2O$$

The valence of chromium in potassium chromate is shown to be 6 by the following diagram of the arrangement of the atoms:



Hence it appears that in the reaction given, chromium has again undergone a change in valence brought about by an oxidizing agent.

Reducing agents produce reverse changes.

These facts represent a general principle which may be stated thus: *Oxidizing agents tend to produce actions in which valence is raised; reducing agents tend to produce actions in which valence is lowered.*

The change of chromates into dichromates, and the reverse changes, do not involve changes of valence, since both salts are derived from the same anhydride.

Nickel

510. Occurrence. — The greater part of the nickel that the world uses comes from the province of Ontario in Canada, and from New Caledonia. The nickel compounds in the ores form only a small part of the whole. The Canadian ore is chiefly a sulphide of iron, containing about 2% each of nickel and copper. Nickel is nearly always a constituent of meteoric iron.

511. Extraction. — The sources of nickel are complex minerals, chiefly sulphides and arsenides mixed with large quantities of other materials. The separation of nickel from such mixtures presents a complex problem. The low percentage of nickel contained in the ore makes it neces-

sary to produce, by methods of concentration, a substance containing a higher percentage of nickel before processes for smelting are carried on. To accomplish this, use is frequently made of the fact that nickel has a greater affinity for arsenic than any of the metals with which it is found associated, and of the fact that nickel stands next to copper in its affinity for sulphur.

If the ore contains no copper, or if the copper is to remain alloyed with the nickel, it is usual to make either (*a*) nickel matte, or (*b*) nickel *speiss*.

Nickel matte is a mixture of sulphides. Nickel speiss is a mixture of arsenides. The process of making these resembles that used for the production of matte (§ 444). They contain from 40% to 50% nickel. In case copper is to be eliminated, one of the simpler methods takes advantage of the affinity of copper for sulphur and of nickel for arsenic. The compounds formed are but slightly soluble in each other.

The nickel matte, or the nickel speiss, is then converted into nickel oxide by oxidation in a reverberatory furnace or a converter.

The nickel oxide is reduced by mixing it with flour paste, rolling and cutting the mixture into small cubes, which are dried, embedded in charcoal, and heated. The nickel cubes thus obtained are suitable for making alloys, but are too impure for nickel ware.

The Mond method is used for the production of pure nickel from the ore. This method is based on the fact that nickel will combine directly with carbon monoxide to form nickel carbonyl, $Ni(CO)_4$. Nickel oxide, produced in smelting the ore, is reduced to nickel in a porous form by heating in the presence of hydrogen. Carbon monoxide at a temperature of 100° C. and a pressure of 15

atmospheres is then passed over the porous nickel to convert it into nickel carbonyl. The vapors of nickel carbonyl are decomposed by heating them to 200° C. under atmospheric pressure. The carbon monoxide is recovered for the conversion of a new lot of nickel into nickel carbonyl. The direction in which the reversible equation

$$Ni + 4\,CO \rightleftarrows Ni(CO)_4$$

runs depends upon temperature and pressure.

512. Properties of Nickel. — Nickel is a hard metal, malleable, possessing a high melting point, and resembling silver in color. It is capable of receiving and retaining a very high polish. Dry air does not attack it. Like cobalt, it dissolves readily in nitric acid, but is only slowly attacked by hydrochloric and sulphuric acids. Nickel-plated ware should never be scoured, but should be cleaned by washing with soap suds and burnishing with a cloth.

Solutions of nickel salts have a beautiful, characteristic green color. Nickel and cobalt resemble iron in being attracted by a magnet. Their chemical properties are also similar to those of iron.

513. Uses. — Nickel is of considerable practical importance because of its silver-white color and of the fact that it does not readily tarnish in air. It is chiefly used as a covering for other metals and in the manufacture of the Edison storage cell. It is deposited by an electrolytic process similar to that used in silver or copper plating. Nickel is a constituent of several important alloys. *Nickel steel*, which contains about 5% nickel, is both hard and tough; it is used in making armor plates for battle ships. *Nickel coins*

contain about one part nickel to three parts copper. *Monel metal*, containing nickel, copper, and iron, is an alloy adapted to many uses on account of its tensile strength. Nickel is used as a catalyst in the hydrogenization of oils.

514. Compounds. — The sulphate, $NiSO_4$, and a double sulphate of nickel and ammonium, $NiSO_4(NH_4)_2SO_4 \cdot 6\,H_2O$, are the salts used as electrolytes in nickel plating.

Cobalt

515. Cobalt Ores. — Cobalt is found as a minor constituent of ores of complex composition. These ores are usually sulphides or arsenides, in which iron is the predominating metal, though they contain copper and nickel as well. Cobalt speiss, $CoAs_2$, is found in Saxony; cobalt glance, $CoAs_2 \cdot CoS_2$, in Norway and Sweden. Cobalt is extracted in the same way as nickel.

516. Properties of Cobalt. — Cobalt is a hard, magnetic metal, malleable and ductile, and capable of receiving a high polish. It is slightly pink. Its melting point, like that of iron, is high. It is used for the same purposes as nickel. It dissolves readily in nitric acid, but is acted on slowly by other acids. Solutions of cobalt salts have a rose color.

517. Cobalt Compounds. — The chloride, $CoCl_2$, and the nitrate, $Co(NO_3)_2$, are of some importance. The chloride has a peculiar property of changing its color when exposed to air of varying humidity. These changes are explained by the fact that the substance forms a number of different compounds with varying amounts of water of crystallization

and passing readily into one another. The less hydrated forms are blue or lavender, while the more hydrated are pink. Heated or exposed to dry air, the pink salt loses water of

FIGURE 217.

When the doll's dress is blue the weather will be fine. The dress is colored with cobalt chloride solution. In dry air this salt loses some of its water of crystallization and is colored blue.

crystallization, and is changed to a blue, less hydrated form. Advantage is taken of this fact to make "sympathetic ink," which is invisible until heated, and for simple apparatus to indicate the amount of moisture in the air (Figs. 217 and 218).

Cobalt nitrate, $Co(NO_3)_2$, is sometimes used in analytical work in testing for certain metals. It unites with certain metallic oxides, forming characteristically colored com-

FIGURE 218.

The dress is pink and the young lady must stay indoors, for rainy weather is threatened.

pounds. Thus aluminum compounds, when converted into the oxide by heating before the blowpipe flame, give a blue coloration when further heated with cobalt nitrate solution, on account of the formation of cobalt aluminate. Similarly, zinc compounds when heated with cobalt nitrate form a double oxide of cobalt and zinc, which is green in color.

SUMMARY

Manganese

Manganese occurs chiefly in pyrolusite, crude manganese dioxide, from which it is obtained by the use of aluminum.

Several alloys of iron and manganese are used in the steel industry. Manganese steel is an important alloy steel.

Manganese dioxide, MnO_2, insoluble, and potassium permanganate, $KMnO_4$, soluble, are two important **oxidizing agents.**

Chromium

Chromium occurs less abundantly than manganese, chiefly as chromite, $Cr_2O_3 \cdot FeO$.

Chromium is used in making **chrome steel,** a very hard and tenacious alloy.

Important **chromium compounds** are: chromic oxide, Cr_2O_3, used as a green pigment; chrome alum, $KCr(SO)_2 \cdot 12\ H_2O$, used in tanning; lead chromate, $PbCrO_4$, used as a yellow pigment; potassium chromate, K_2CrO_4, and potassium dichromate, $K_2Cr_2O_7$, used as oxidizing agents

Chromium, like manganese, forms **two classes of compounds.** In one, it shows the properties of a metal; in the other, those of a non-metal. In the former it has a lower valence than in the latter.

The change in valence in such elements as manganese and chromium is brought about by oxidizing agents or reducing agents. **Oxidizing agents tend to raise valence, reducing agents to lower it.**

Nickel

When a **nickel ore** contains arsenic, nickel will take arsenic from the other metals until it is satisfied. During the process a portion of the other metals will be oxidized and the oxides will

pass into slag. When copper is not present a similar statement is true concerning the behavior of nickel towards sulphur.

A substance rich in nickel arsenide is known as **nickel speiss.**

Nickel matte is a substance rich in nickel sulphide.

Nickel oxide is obtained from nickel speiss or from nickel matte by oxidation in a furnace.

Cubes of somewhat impure nickel are formed by reducing nickel oxide by mixing it with flour and heating in charcoal.

Pure nickel is obtained by making use of the facts that carbon monoxide under pressure and at a temperature of 100° C. converts nickel into nickel carbonyl ($Ni(CO)_4$) and that the vapor of nickel carbonyl decomposes at 200° C.

Nickel **does not tarnish in dry air** and is **used** for making alloys and as a protective coating for iron.

Cobalt

Metallic cobalt is like nickel in its properties and uses.

Important **cobalt compounds** are the chloride, nitrate, and sulphide.

EXERCISES

1. How is manganese obtained in the free state from pyrolusite?

2. Why is spiegeleisen used in making Bessemer steel?

3. Why is manganese dioxide mixed with carbon in a dry cell?

4. Which is the easier to preserve, potassium manganate or potassium permanganate? Why?

5. What qualities does chromium give to steel? For what purposes is chrome steel suited?

6. Explain the relation between potassium chromate and potassium dichromate.

7. Why is the change of chromous into chromic chloride spoken of as oxidation?

8. What is monel metal?

9. Why is iron often plated with nickel?

10. Name an acid in which nickel dissolves readily.

11. Name three metals that are attracted by a magnet.

12. Explain the action of sympathetic ink.

CHAPTER XXXVII

THE PERIODIC LAW

518. Early Attempts at Classification. — The discovery of new elements and the investigation of their properties led the earlier chemists to recognize the existence of certain families or groups of elements. It was not until 1860–1870, however, that any system of classifying the elements received recognition. In 1863–1864, Newlands, an Englishman, announced that the elements showed regularity when arranged in order of their atomic weight, in that the properties of each element seemed to be repeated in a measure by those of the eighth element following it. This relation is called the *law of octaves*. The work of Newlands passed unnoticed at the time. In 1869, Mendelejeff, a Russian chemist, aroused great interest in scientific circles by bringing forward a system of classification that for the first time brought all the elements into a comprehensive scheme of relationship, based upon their atomic weights. Lothar Meyer, a German chemist, worked out a similar classification about the same time. The system to-day bears the name of Mendelejeff, however, since it was the Russian chemist who elaborated and successfully defended his system against the many attacks made upon it.

519. Periodic Law. — Beginning with lithium, let us arrange the elements in the order of their atomic weights:

Lithium	Glucinum	Boron	Carbon	Nitrogen	Oxygen	Fluorine
7	9	11	12	14	16	19

Lithium is a metal with strong basic properties; glucinum, Gl, is less basic; boron has some metallic properties, but generally acts like a non-metal; carbon forms weak acids; nitrogen, oxygen, and fluorine are progressively stronger in their acid-forming properties. Hence, the seven elements show a gradation in properties from a pronounced metal, or base forming element, to one that has the opposite, or acid forming character. A similar transition can be shown for other properties as we pass from lithium to fluorine. Thus the properties seem to vary with the atomic weights, or, in mathematical language, the properties are functions of the atomic weights. Sodium, the eighth element after lithium, closely resembles it, and may be placed directly beneath as the beginning of another horizontal row:

Lithium	Glucinum	Boron	Carbon	Nitrogen	Oxygen	Fluorine
7	9	11	12	14	16	19
Sodium	Magnesium	Alumi-num	Silicon	Phosphorus	Sul-phur	Chlorine
23	24	27	28	31	32	35.5

Magnesium resembles glucinum in its properties, and the characteristics of boron recur modified in aluminum. That is, the eighth element repeats the properties of the one taken as the first. Silicon, then, should be like carbon, and phosphorus should resemble nitrogen. These we know to be facts. Since the properties recur or are repeated at regular intervals, the properties are said to be periodic; or, as Mendelejeff expressed it, "a periodic repetition of properties is obtained if all the elements be arranged in the order of the atomic weights."

Dimitri Ivanovitch Mendelejeff (1834–1907) was born in Tobolsk, Siberia. Through the efforts of his mother, who established a glass works, he received an excellent education in Tobolsk and St. Petersburg. He spent the greater portion of his life as Professor of Chemistry in the University of St. Petersburg, and to him Russia owes the training of two generations of chemists, as well as the development of its petroleum and other chemical industries. Although there was no section of the chemical science of his time which was not enriched by his contributions, the fame of Mendelejeff rests secure on the setting forth and establishment of the Periodic Law.

520. Long and Short Periods. — The table on page 516 is arranged according to the principle of classification just given. Omitting for the present the first vertical column marked Series 0, the seven elements, from lithium to fluorine, form a horizontal series known as a *short period.* The set of elements from sodium to chlorine make the second short period. Beginning in the next line with potassium, it is found that the metallic properties do not disappear so rapidly as in the first and second short periods. Manganese, the seventh element, has some well-marked metallic properties. Iron is not placed under potassium, but is put in an eighth series together with cobalt and nickel. There is a gradual increase in the metallic properties as we pass through these three elements to the more metallic copper. The elements from copper to bromine show a gradual decline in the metallic properties and an increase in the acid properties until the strongly acid element bromine is reached. Hence we find that this time it takes seventeen elements to make a complete transition from metallic to non-metallic elements. This is known as a *long period.* Each long period is subdivided into two sub-periods, each of which, in a measure, shows the same transitions that were observed in the first and second short periods. (See table, page 516.) The elements from rubidium to iodine constitute the second long period.

521. Families or Groups of Elements. — An inspection of the periodic table will show that all the elements in one of the vertical series have certain resemblances. The relationship, however, is much closer in some cases than in others. Thus, in Series II, calcium, strontium, and barium are more closely allied to each other than they are to magnesium, zinc,

	Series 0	Series I	Series II	Series III	Series IV	Series V	Series VI	Series VII	Series VIII
	R	R_2O ROH	RO $R(OH)_2$	R_2O_3 $R(OH)_3$	RO_2 $R(OH)_4$	R_2O_5 RO_4H_3	RO_3 RO_4H_2	R_2O_7 RO_4H	←Oxide ←Hydroxide
1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	
2	Ne 20	Na 23	Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.5	
3	A 39.9	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56 Co 58.9 Ni 58.7
4	—	Cu 63.6	Zn 65.4	Ga 70	Ge 72.5	As 75	Se 79.2	Br 80	
5	Kr 82.9	Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 93.5	Mo 96	—	Ru 101.7 Rh 103 Pd 106.7
6	—	Ag 108	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.5	I 127	
7	Xe 130	Cs 133	Ba 137.4	La, etc. 139		Ta 181.5	W 184	—	Os 191 Ir 193 Pt 195
8		Au 197	Hg 200	Tl 204	Pb 207	Bi 208	Po 210	—	
9	Nt 222.4	—	Ra 226	Ac	Th 232	Ux_2 234	U 238.5		

The above is Mendelejeff's table, arranged in the light of limitations imposed by the atomic numbers.

cadmium, and mercury. These last four elements form a closely related group. That is, the more closely related elements are not successive, but alternate in a vertical series. The result of this alternate arrangement is to divide each vertical series into two families or groups. In Series VI, chromium and molybdenum are in one family, while sulphur, selenium, and tellurium form the other. The halogen elements, chlorine, bromine, and iodine, in Series VII, afford one of the best examples of a closely related group.

At the head of each vertical series are placed some general formulas for the oxides and hydroxides of the elements in the series beneath. R is the general symbol for an atom of the element under consideration. Thus in Series I the general formula of the oxide is R_2O, and we have the oxides Li_2O, Na_2O, K_2O, Cu_2O, and so on.

These general formulas may be extended to include other compounds, as the chloride, nitrate, and sulphate:

	SERIES I		SERIES II	
	Formula	Illustration	Formula	Illustration
Oxide	R_2O	K_2O	RO	CaO
Hydroxide	ROH	KOH	$R(OH)_2$	$Mg(OH)_2$
Chloride	RCl	KCl	RCl_2	$HgCl_2$
Nitrate	RNO_3	KNO_3	$R(NO_3)_2$	$Zn(NO_3)_2$
Sulphate	R_2SO_4	K_2SO_4	RSO_4	$BaSO_4$

	SERIES III	
	Formula	Illustration
Oxide	R_2O_3	Al_2O_3
Hydroxide	$R(OH)_3$	$Al(OH)_3$
Chloride	RCl_3	$AlCl_3$
Nitrate	$R(NO_3)_3$	$Al(NO_3)_3$
Sulphate	$R_2(SO_4)_3$	$Al_2(SO_4)_3$

It can be seen from the study of these general formulas that there is a regular increase in valence as we proceed from the first series to the seventh.

522. Position of the Inert Gases and of Hydrogen. — With the discovery of argon and other inert gases, considerable discussion arose as to their proper place in the periodic system. The atomic weights of these elements indicate that they form another series placed at the left of Series I. Since no compounds of these elements are known, their valence can properly be said to be 0. Accordingly, it has been deemed best to call this Series 0. The elements in Series 0 occupy spaces corresponding to vacancies in Series VIII. Including these inert elements, the first two short periods have eight elements each, while the first long period has eighteen.

It will be noticed that hydrogen is not placed in the table given. Since it has the smallest atomic weight, its natural position would be at the beginning of the classification. If however, it were placed in Series 0, it would be classed with the inert elements from which it differs decidedly in its properties. Although hydrogen furnishes univalent positive ions, like the alkali metals in Series I, it does not have the physical properties of a metal. Hence it does not fit well into that series. The position of hydrogen is so uncertain that it is omitted from many periodic tables.

523. Value of the Periodic System. — *Mendelejeff's system has been of great value in predicting the discovery of new elements.* In fact, in the years immediately following the announcement of the law, when its validity was so much questioned, the fulfillment of Mendelejeff's predictions as to the existence and properties of elements then unknown gave striking evi-

dence of the correctness of the new system of classification. The table following shows the predictions and their verification in the case of an element which Mendelejeff called *eka-aluminum*, and which is now known as *gallium:*

Properties	Predicted	Discovered
Atomic weight	About 69	69.9
Melting point	Low	30.1°
Specific gravity	About 5.9	5.93
Action of air	None	Slightly oxidized at red heat
Action on water	Decomposes at red heat	Decomposes at high temperatures

The predictions by Mendelejeff and their subsequent verification were equally striking in the cases of eka-boron (scandium) and eka-silicon (germanium), and did more than anything else to secure a general acceptance of his system.

The second use of the classification is in the adjustment and revision of atomic weights. In the early days of the classification, many of the elements were improperly placed. It was suggested that this might be due to incorrect values for the atomic weights. This led to more accurate determinations of the atomic weights. In many cases, results were obtained that permitted the elements to be placed in the table according to their proper relationships. Chemical research has been greatly stimulated in the effort to get accurate revisions of atomic weights.

The development of a systematic study of the elements has been the greatest service of the periodic law. A knowledge of relationships has simplified the determination of the physical and chemical properties not only of the elements but of their compounds. Although the system of Men-

A Periodic Classification of the Elements According to Thomsen.

delejeff is not perfect, and no exact numerical relations have been found, the periodic classification is of great aid to the student of descriptive chemistry.

524. Atomic Numbers. — An important advance in the classification of the elements was the idea of atomic numbers [1] introduced in 1913 by Moseley, an Englishman. The life of this brilliant scientist was unfortunately sacrificed at the Dardanelles early in the Great War.

His atomic numbers were obtained by the use of X-rays. When a current of electricity is passed through a tube from which the air has been exhausted, cathode rays are produced. A stream of cathode rays falling on the surface of a metal excites it so that it gives off vibrations known as X-rays. These rays are like light waves, except that the wave lengths of X-rays are very much shorter. The X-rays are characteristic of the metal from which they come, and when reflected from the face of a crystal form spectra with well-marked lines. From photographs of the spectra, it is possible to determine the rate of vibration per second (frequency number) of the rays producing the well-marked lines. Calculations from these frequency numbers give a factor or value known as "Q" for each element.

If we arrange the elements in the order of the "Q" values, we note that the successive values differ approximately from each other by unity, and that the elements themselves fall into the general order of their chemical

[1] In the table on the opposite page, atomic numbers, obtained by a study of X-ray spectra, are arranged in a way that shows family relationships with great clearness. The dotted lines indicate sub-group relationships without the undue emphasis shown in the Mendelejeff system. It appears that there are 92 types of elements and that only 3 remain undiscovered, but a doubtful one shows in the table.

properties. Placing hydrogen first and giving it the atomic number 1, the atomic numbers of the succeeding elements, placed in the order of their "Q" values, are helium 2, lithium 3, glucinum 4, boron 5, carbon 6, nitrogen 7, oxygen 8, fluorine 9, and so on.

As shown in § 122, the atomic number is believed to be precisely the same as the number of electrons outside the nucleus of the atom. *The atomic number of an element denotes its position in the series of elements, as determined by its X-ray spectrum.*

Atomic numbers may be obtained for the liquid and the gaseous elements. A compound of such an element is used and from it an X-ray spectrum is obtained. Thus the frequency number of chlorine can be found from the examination of the X-ray spectrum of potassium chloride. The characteristic lines of potassium in such a spectrum are known; the other lines then must belong to the chlorine.

525. Advantages of the Atomic Numbers. — According to the order of their increasing atomic weights, several elements cannot be placed in the proper group in the periodic table, *e.g.* argon, 39.9, and potassium 39; iron 56, cobalt 58.9, and nickel 58.7; tellurium 127.5, and iodine 127. The atomic numbers of these elements correspond to their arrangement according to their chemical properties, and insure the proper placing of the elements in a periodic classification, viz., argon 18, potassium 19, iron 26, cobalt 27, nickel 28; tellurium 52, iodine, 53. (See table on page 520.)

The gaps in the atomic numbers clearly indicate the number of new elements that may be discovered; for example, between molybdenum, 42, and ruthenium, 44, there is

room for but one element. The actual number of the metals of the rare earths and their proper placing in the Periodic Table have always been baffling problems. The atomic numbers of Moseley indicate, however, that there should be but 15 such elements between lanthanum and ytrium. After the missing rare earth metals are found, chemists will not waste their time searching for elements of this group that cannot exist. Neither will they believe that the spectra of some of the heavenly bodies give reliable evidence of celestial elements, unless they can fit these into the scheme of the atomic numbers. According to Moseley, the total number of possible elements should be 92, ranging from hydrogen to uranium.

The great service, however, of atomic numbers is the explanation they give of the nature and cause of chemical action. At least with the first twenty cases, we can form an accurate idea of the entire chemical nature of an element by knowing its atomic number.

SUMMARY

The **principle of the Mendelejeff classification** of the elements is that "a periodic repetition of properties is obtained if all the elements be arranged in the order of the atomic weights."

While the elements in the **horizontal series** show a gradual transition in properties, the most closely related **families** or groups are arranged alternately in the vertical series.

The **Periodic System** has been of great value in (*a*) predicting the discovery of new elements, (*b*) the adjustment and revision of atomic weights, (*c*) the development of a systematic study of the elements.

The **atomic number** of an element denotes its position in the series of elements, as determined by its X-ray spectrum.

EXERCISES

1. Show that there is in the second short period a transition from a strongly metallic element to a pronounced acid element.

2. Show by illustrations that the Mendelejeff classification is a periodic one.

3. Using symbols, indicate two families of elements in each of the following vertical series — II, IV, VI.

4. Give formulas for the oxide, hydroxide, sulphate, nitrate, and chloride of indium (In).

5. What was the difficulty in placing the inert gases in the table on their discovery? How were they later placed?

6. What two uses of the table were of great value in securing its acceptance by chemists?

7. How may a student use the table profitably in the study of chemistry?

8. What are atomic numbers?

9. Cite some instances of elements that are more logically placed in the atomic number table than in the Mendelejeff table.

10. How is it shown by atomic numbers that there is not an unlimited number of elements to be discovered?

11. What element would the undiscovered element following molybdenum most closely resemble?

12. Why should many compounds of carbon and silicon be expected to be much alike?

13. Why should the compounds of calcium, strontium, and barium resemble one another more closely than they do the compounds of magnesium, zinc, and mercury?

14. Name in each case a family of elements that show (*a*) the best electrical conductivity, (*b*) strong basic properties, (*c*) strong acid forming properties.

15. Why should you expect from the Periodic Table that magnesium would be related to sodium, calcium, and zinc?

CHAPTER XXXVIII

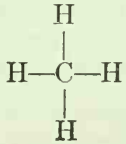
CARBON COMPOUNDS

526. Organic Chemistry. — The term "organic chemistry" owes its origin to the notion that a force different from that governing the mineral kingdom was necessary for the formation of nearly all compounds produced by plants and animals. This belief was overthrown by Wohler in 1828, but organic chemistry is still the name commonly applied to the study of carbon compounds. Carbon unites with other elements to form a very large number of compounds, most of which have a complex structure. As a rule, carbon compounds are only slightly ionized by water.

527. Structural Formulas. — Little advance was made in the study of carbon compounds until chemists began to represent the arrangement of the atoms in the molecule by structural formulas. A structural formula may be considered as a map of the molecule.

In a structural formula, each valence is represented by a dash leading from the symbol of the element considered. The fact that carbon has a valence of four is represented by

H — is used to show that hydrogen has a valence of one. The structural formula for methane, the simplest compound of carbon and hydrogen, is



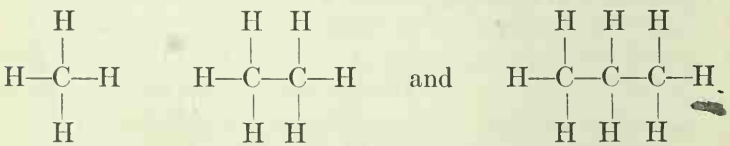
in which four dashes, or *bonds*, as they are commonly called, lead from the symbol for carbon, and one bond leads from each symbol for hydrogen. As no bond exists free, or unattached, the valence of carbon is satisfied by hydrogen.

528. Reason for the Large Number of Carbon Compounds. — Atoms of nitrogen to a limited extent have the power of uniting with other nitrogen atoms to form nuclei. A similar statement is true in the cases of several other elements. Carbon possesses this power to an almost unlimited extent. The high valence of carbon, and the fact that carbon atoms readily unite with each other to form stable nuclei, account for the very large number of carbon compounds that are known to exist.

HYDROCARBONS

It is customary to commence the study of organic chemistry with a consideration of hydrocarbons. From these all carbon compounds are actually or theoretically derived. *A hydrocarbon is a compound composed of hydrogen and carbon.*

529. Methane or Paraffin Series. — This series receives its names from its first member, methane, and from the fact that paraffin wax is a mixture of the higher members of the series. The structural formulas of the first three members of the series and the names of the compounds are:



Methane Ethane Propane

The series is called a *saturated series* because it contains no compound in which two carbon atoms are joined by more than one bond. Each molecule is incapable of holding more hydrogen; in other words, it is saturated with hydrogen.

The names, empirical formulas, and some of the physical constants of eight members of the paraffin series are given in the following table:

PARAFFIN SERIES

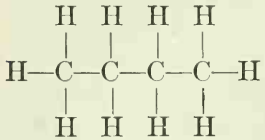
	Formula	Molecular Weight	Boiling Point	Freezing (or Melting) Point	
Methane	CH_4	16	− 164°C.	—	Ordinarily gaseous
Ethane	C_2H_6	30	− 89.5	—	
Propane	C_3H_8	44	− 38	—	
Butane	C_4H_{10}	58	+ 1	—	
Pentane	C_5H_{12}	72	36	—	Liquid
Hexane	C_6H_{14}	86	71	—	
Hexadecane	$C_{16}H_{34}$	226	288	18°	Solid
Octodecane	$C_{18}H_{38}$	254	317	28	

With increasing molecular weight, there will be noticed a rising of the boiling point and the tendency to assume the solid form.

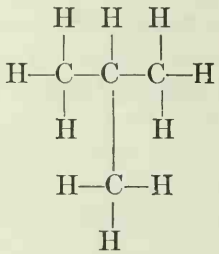
If n is used to stand for the number of carbon atoms in the molecule of a hydrocarbon, the general formula for the paraffins is written C_nH_{2n+2}. The formula for any member of the series can be readily obtained when the number of carbon atoms in the molecule is known. Thus, hexane contains 6 carbon atoms; n, therefore, equals 6, and the number of hydrogen atoms in a molecule of hexane is $(2 \times 6) + 2$, or 14. The formula for hexane is C_6H_{14}.

It will be observed that the formula for each member of the series differs from that of the preceding member by CH_2. Such a series is called an *homologous series.*

530. Isomers. — There is only one methane, one ethane, and one propane, but as soon as butane is reached, it becomes possible to group the atoms in more than one way. This results in the structural formulas:



Normal Butane



Isobutane

Both of the above compounds are known. In the normal butane, no carbon atom is joined to more than two carbon atoms, while in isobutane one of the four carbon atoms is joined to three carbon atoms. Butane and isobutane are known as *isomers*.

Isomers are compounds having the same percentage composition, but possessing different properties on account of differences in the arrangement of the atoms in the molecules.

As the number of carbon atoms increases, the number of isomers theoretically possible increases very rapidly, so that when the number of carbon atoms in the molecule is 15, the number of isomers theoretically possible is over 4000.

531. Methane is a colorless, odorless gas, which, when pure, burns with a slightly luminous flame. It is produced during the changes that take place in vegetable material under water, and frequently the gas may be seen bubbling through the water. The fact that this decomposition takes place in marshes caused methane to be called *marsh gas*.

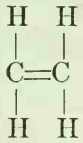
Methane mixed with air forms explosive mixtures and is

frequently a source of danger in coal mines, where it is called *fire damp*. Methane is the chief constituent of natural gas.

532. Unsaturated Hydrocarbons. — *An unsaturated carbon compound contains at least two atoms of carbon that are joined by more than one bond.*

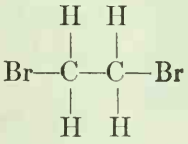
533. Ethylene or Olefiant Gas Series. — This series is an homologous series, the members of which contain two carbon atoms that are joined by a double bond. The general formula for the members of the series is C_nH_{2n}.

534. Olefiant gas, or ethylene, C_2H_4, the first member of the series, has the structural formula:



It is a valuable constituent of illuminating gas on account of the luminosity that it gives to the flame.

The olefins are much more active chemically than the paraffins. Ethylene readily combines with *two* atoms of bromine to form the saturated compound



ethylene bromide. Since ethylene unites with two atoms of bromine and never with one atom, its molecule is believed to contain two carbon atoms joined by a double bond.

535. Acetylene Series. — This is an homologous series whose members contain two carbon atoms joined by three

bonds. The general formula for the series is C_nH_{2n-2}. The series is named from its first member acetylene, H—C≡C—H.

Acetylene has already been mentioned (§ 324) as a gas resulting from the reaction between calcium carbide and water.

$$\begin{array}{c} Ca \\ \diagup\diagdown \\ C\equiv C \end{array} + 2\,HOH \longrightarrow H{-}C\equiv C{-}H + Ca(OH)_2$$

The reaction is employed for the production of acetylene gas for use as an illuminating gas in rural districts, in bicycle lamps, and in some types of automobile lamps, and to make acetylene for use in the oxy-acetylene blowpipe. In order to have acetylene burn with a clean flame, the gas must be mixed with an unusually large volume of primary air. Acetylene burners utilize the principles of the bunsen burner and the flat flame or fishtail burner (Figs. 134 and 219).

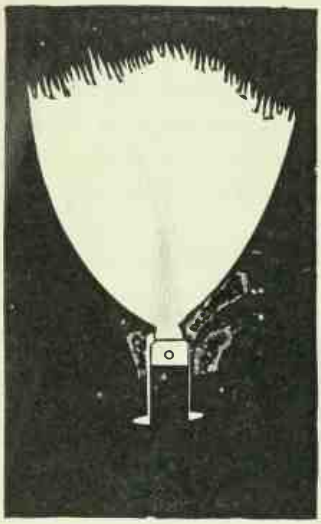
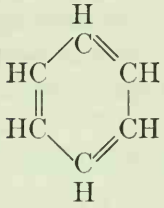


FIGURE 219.

An acetylene flame is characterized by the brilliant whiteness of its light.

536. Benzene Series. — Of the many series of hydrocarbons known to exist in addition to the three already mentioned, only one, the benzene series, will be considered. The benzene series is an homologous series whose members have the general formula C_nH_{2n-6}.

Benzene is the first member of the series. Its structural formula is



Benzene is one of the many compounds called *ring compounds* because their structural formulas show a ring formation. The benzene series is frequently spoken of as the *aromatic series* because many of its members possess an aromatic odor. Unlike the paraffins, the ring hydrocarbons react readily with nitric and sulphuric acids, forming important compounds used in the preparation of dyestuffs and in explosives.

537. Benzene, often called benzol, is produced as crude benzene, during the destructive distillation of soft coal, and most of it is recovered from the gases of coke ovens, and from coal gas during its purification for use as an illuminating gas. It is also obtained from the fraction of light tar oils that boils at temperatures between 80° C. and 85° C. Benzene, C_6H_6, is a colorless, volatile liquid, lighter than water, and has a characteristic odor. It is obtained by the distillation of crude benzene. Benzene burns with a smoky flame. It is a good solvent for fats and resins but its principal use is for the production of more complex carbon compounds.

538. Toluene (*toluol*), $C_6H_5 \cdot CH_3$, the second member of the benzene series, resembles benzene in its properties. It

came into prominence during the Great War, because from it was made the powerful explosive trinitrotoluene, T.N.T., $C_7H_5(NO_2)_3$. "Amatol" contains 20% of T.N.T. and 80% of ammonium nitrate. It was being prepared on a large scale for use as an explosive when the war ended.

Halogen Substitution Products

539. Substitution is the replacement of an element or a radical in a compound by another element or radical.

A halogen substitution product is a compound derived from a hydrocarbon by exchanging one or more atoms of hydrogen for a corresponding number of halogen atoms. It is not necessary that the substitution product be actually made in this way. The chlorine substitution products of methane are:

CH_3Cl, *monochlor*methane
CH_2Cl_2, *dichlor*methane
$CHCl_3$, *trichlor*methane (chloroform)
CCl_4, *tetrachlor*methane (carbon tetrachloride)

540. Chloroform. — Trichlormethane, *chloroform*, $CHCl_3$, is prepared by distilling alcohol or acetone with bleaching powder, and by the reduction of carbon tetrachloride. Chloroform is a heavy, colorless, easily flowing liquid, having a characteristic ethereal odor and a sweet taste. It is very slightly soluble in water. Chloroform is an important solvent and, when pure, a safe and most valuable anæsthetic.

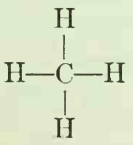
541. Carbon Tetrachloride, CCl_4, is prepared by the action of chlorine on carbon disulphide in the presence of a catalytic agent. The production of carbon tetrachloride and other substitution products from natural gas, which is largely composed of methane, has attracted much attention.

Carbon tetrachloride is a low boiling, non-flammable liquid and is a good solvent for grease. These properties make it a valuable substitute for gasoline in the removal of grease and paint from clothing. It is also extensively used in certain types of fire extinguishers. When a stream of the liquid is directed against a burning substance, the heat causes it to evaporate instantly, forming a heavy gas that displaces the air in contact with the combustible material.

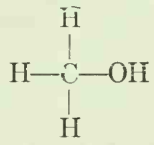
542. Iodoform, CHI_3, is the iodine compound corresponding to chloroform, and is prepared by the reaction of alcohol and iodine in the presence of an alkali. It is a light yellow powder with a characteristic, disagreeable odor. Iodoform is useful as an antiseptic.

Alcohols

An alcohol is a hydroxyl (OH) substitution product. The alcohols may be considered as being derived from hydrocarbons by the substitution of one or more hydroxyl groups for a corresponding number of hydrogen atoms. As a rule, two hydroxyl groups do not remain attached to the same carbon atom. An alcohol may also be considered as the first step in the oxidation of a hydrocarbon, the oxygen atom entering the molecule between an atom of hydrogen and an atom of carbon, as in the case of methyl alcohol, CH_3OH, which is an alcohol of methane, CH_4.



Methane



Methyl Alcohol

543. Methyl Alcohol is one of the products obtained by the destructive distillation of wood. Impure methyl alcohol is sold as *wood alcohol*. Pure methyl alcohol has an odor and taste resembling ordinary alcohol. It is a poisonous substance, and many cases of blindness and death have occurred as a result of drinking beverages containing methyl alcohol. It should never be employed for alcohol rubs. Wood alcohol is used as a solvent in making polishes, lacquers, and varnishes and also in the manufacture of aniline dyes. Wood alcohol burns with a flame of high heat value, and is, therefore, suitable for use in alcohol stoves. It is also called *methanol*.

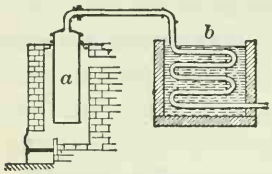
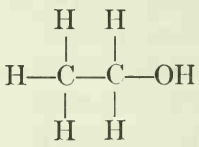


FIGURE 220.

Wood is destructively distilled in (*a*). The liquid products are condensed in (*b*). Wood alcohol is an important product.

544. Ethyl Alcohol, *alcohol*, grain alcohol, C_2H_5OH,



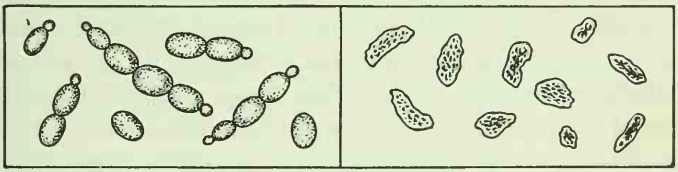
The term "alcohol" when unqualified always signifies ethyl alcohol.

Alcohol is always prepared commercially by the fermentation of certain sugars. Yeasts are one-celled plants present in the air. They secrete catalysts (enzymes) one of which, zymase, has the power of causing a number of sugars, for example glucose, to change to alcohol and carbon dioxide:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2\uparrow$$

The carbon dioxide evolved during this change frequently causes foam to appear on the fermenting substances. When preserves ferment, they are commonly said to "work." In general, *fermentation* is a chemical change brought about by living organisms, or by catalytic agents, called *enzymes*, secreted by them.

Ordinary alcohol is made in large quantities from grains or potatoes by processes of fermentation. The starch in these substances is converted by enzymes into glucose or other fermentable sugars. After alcoholic fermentation has taken



a *b*

FIGURE 221.

Yeast is a plant which secretes zymase, a substance that acts catalytically on glucose, converting it into alcohol and carbon dioxide. In *a* we have the living cells, in *b* the dead cells, both highly magnified.

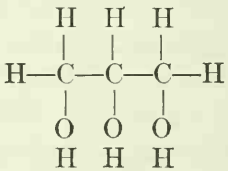
place, the alcohol is separated from the fermented substance by distillation. By fractional distillation a liquid containing about 95% of alcohol is obtained. When alcohol of greater purity is desired, the remaining water mixed with it is removed by calcium oxide, which combines with the water to form calcium hydroxide. *Absolute alcohol* is obtained by distillation from this mixture of alcohol and calcium hydroxide.

The physical properties of ethyl alcohol closely resemble those of methyl alcohol. Alcohol burns with a clean, blue flame of high heat value. It is the constituent of alcoholic beverages to which they owe their intoxicating properties. *Tinctures* are solutions in which alcohol is the solvent.

Alcohol is used extensively in making fluid extracts, in the preparation of lacquers, dyes, and pharmaceutical preparations. Since it can be made cheaply from cellulose, its industrial use as a fuel is likely to increase.

545. Denatured Alcohol. — A completely denatured alcohol is ethyl alcohol mixed with small quantities of substances that are added to produce a poisonous solution having a disagreeable odor. Methyl alcohol, benzol, and pyridine are some of the substances used for denaturing. The United States aims to encourage the use of alcohol for industrial purposes. A completely denatured alcohol prepared according to any one of the formulas authorized by law is sold without restrictions and is tax free. Neither does the United States collect a tax on specially denatured alcohols suitable for use in industries, but it regulates the distribution and use of such alcohols.

546. Glycerine, $C_3H_5(OH)_3$, is a trihydroxyl alcohol of propane.

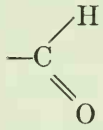


Its preparation will be considered in connection with soap-making (§ 557). Glycerine is a thick liquid having a sweet taste. It is very hygroscopic and dissolves a great variety of substances. Large quantities are consumed in the manufacture of nitroglycerine. Glycerine is extensively used in cosmetic and medicinal preparations. It is also used in the manufacture of printer's rolls and inks for use

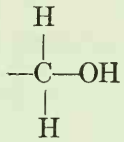
with rubber stamps. The hygroscopic properties of glycerine cause it to be used to keep tobacco moist, and to keep leather soft.

ALDEHYDES

An aldehyde is a carbon compound containing the group

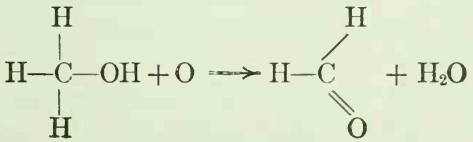


Aldehydes result from the partial oxidation of alcohols in which the hydroxyl group is attached to a carbon atom bearing two hydrogen atoms, or, in other words, from alcohols containing the group



It is supposed that during the partial oxidation of such alcohols two hydroxyl groups become attached to the same carbon atom, and that the unstable compound thus formed at once decomposes, yielding water and an aldehyde.

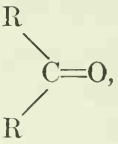
547. Formic Aldehyde (formaldehyde) is prepared by the oxidation of methyl alcohol. The oxidation is effected by passing a mixture of methyl alcohol vapor with air over a hot spiral of copper, or over a hot braid of asbestos:



Formaldehyde, at ordinary temperatures, is a gas that has a very pungent odor and causes the eyes to smart. A water solution of formaldehyde containing about 40% of the gas is sold as *formalin*. When an aqueous solution of formaldehyde is evaporated over concentrated sulphuric acid, some of the formaldehyde molecules combine with each other to form a white solid, *paraformaldehyde* or *formacone*. Paraformaldehyde, on being heated, changes to formaldehyde. In the form of a gas, or in water solutions, formaldehyde is a valuable germicide and is largely employed as a disinfectant. Water solutions of formaldehyde are used for the preservation of anatomical specimens, for the hardening of the gelatin films of photographic plates, for changing casein to an insoluble substance, and for various other industrial uses.

KETONES

Ketones are carbon compounds having the general formula



in which R stands for groups having the general formula C_nH_{2n+1}.

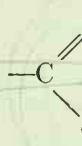
548. Acetone, CH_3COCH_3, is made by the dry distillation of calcium acetate. It is a colorless liquid, having a fruity odor. It is an excellent solvent for resins, gums, and acetylene, and is used in the manufacture of chloroform and synthetic indigo.

Prest-O-Lite is acetylene dissolved in acetone. Prest-O-Lite cylinders are filled with asbestos that has been soaked

in acetone. Acetylene is forced into the cylinder and dissolves under pressure in the acetone. When the valve of the cylinder is opened, acetylene passes out of solution and escapes as a gas from the cylinder.

ORGANIC ACIDS

549. Organic Acids are characterized by the group



called the *carboxyl group*. The hydrogen of the carboxyl group can be replaced by a metal and is therefore acid hydrogen. Several important organic acids of the paraffin series contain but one replaceable hydrogen atom and therefore are monobasic acids. Consequently they have the general formula $C_nH_{2n+1}COOH$. If the numerical value of n is known, the formula for the acid is readily calculated by use of the general formula. The value of n in a few cases is given in the table below.

Name of Acid	Value of n	Formula of Acid
Formic acid	0	$HCOOH$
Acetic acid	1	CH_3COOH
Butyric acid	3	C_3H_7COOH
Palmitic acid	15	$C_{15}H_{31}COOH$
Stearic acid	17	$C_{17}H_{35}COOH$

550. Acetic Acid is produced when hard cider changes to vinegar. Sweet cider contains sugars, fruit sugar being the

principal one. Yeast plants from the air fall into sweet cider and cause alcoholic fermentation to take place, during which the sweet cider changes to hard cider.

Courtesy of Amer. Museum of Natural History

FIGURE 222.

A photograph of acetic acid bacteria (magnified 4000 diameters).

$$C_6H_{12}O_6 \longrightarrow 2\,CO_2\uparrow + 2\,C_2H_5OH$$

On continued exposure to air, acetic acid bacteria, "mother of vinegar," having entered the cider from the air, cause the alcohol contained in the hard cider to combine with oxygen and produce acetic acid and water, by acetic acid fermentation.

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$$

Commercial acetic acid is obtained from the destructive distillation of wood.

551. Oxalic Acid, $\begin{matrix}COOH\\|\\COOH\end{matrix}$ or $H_2C_2O_4$, is obtained by heating sawdust in the presence of caustic soda, neutralizing a water solution of the product with calcium hydroxide, and then decomposing the calcium oxalate with sulphuric acid. Commercial oxalic acid contains water of crystallization as shown by the formula $H_2C_2O_4 \cdot 2\,H_2O$. Sublimed oxalic acid is anhydrous. Oxalic acid is a mild reducing agent and, on this account, is frequently used in the removal of fresh iron rust and ink spots from white cloth, and for bleaching straw hats. It is also used for cleaning copper and brass. Oxalic acid is an important reagent in analytical laboratories and is used in calico printing, dyeing, and tanning.

The fact that *oxalic acid is a poison* should not be forgotten when the acid is kept in the house and when it is used.

552. Important Fruit Acids. — *Tartaric Acid*, $H_2(C_4H_4O_6)$, is made from crude cream of tartar which deposits on the side walls of wine vats during the fermentation of grape juice. Potassium acid tartrate, $KH(C_4H_4O_6)$, is *cream of tartar*.

Citric Acid, $H_3(C_6H_5O_7)$, is found in the juices of lemons, oranges, limes, gooseberries, and many other kinds of fruit.

ESTERS

Esters are widely distributed in nature and are of great economic and æsthetic importance. They are called *ethereal salts* because many of them are volatile, have delicate odors resembling those of flowers and fruits, and because all esters are analogous to inorganic salts in constitution.

553. Formation of Esters. — The reaction between an alcohol and an acid closely resembles the reaction between a base and an acid in neutralization. When sodium hydroxide is neutralized with nitric acid, water and sodium nitrate are the products.

$$NaOH + HNO_3 \longrightarrow HOH + NaNO_3$$

When ethyl alcohol is esterified with nitric acid, water and ethyl nitrate are formed.

$$C_2H_5OH + HNO_3 \rightleftharpoons HOH + C_2H_5NO_3$$

An ester is the product other than water formed when an alcohol reacts with an acid, the alcohol taking the part of a base.

The formation of an ester differs from neutralization in some important respects. Unlike neutralization, esterification proceeds very slowly at ordinary temperatures, and the reaction is reversible. To cause the reaction to proceed to completion, one of the products (water) is generally removed from the field of action by use of a dehydrating agent. Sulphuric acid is the dehydrating agent most commonly employed. In chemical behavior with water, esters closely resemble salts formed by the neutralization of a weak acid or of a weak base. The student will remember that such salts easily undergo hydrolysis (§ 187), that is, the process of neutralization is to some extent reversed.

554. Esters of Inorganic Acids. — Two of the well-known esters of inorganic acids are *ethyl nitrite*, $C_2H_5NO_2$, an alcoholic solution of which is sold as "sweet spirits of niter"; and the powerful explosive *nitroglycerine*, which is glyceryl nitrate, $C_3H_5(NO_3)_3$.

Nitroglycerine is manufactured by slowly and carefully injecting glycerine into a thoroughly cooled mixture of concentrated nitric and sulphuric acids.

$$C_3H_5(OH)_3 + 3\ HNO_3 \longrightarrow 3\ HOH + C_3H_5(NO_3)_3$$

During the process, the liquid mixture is cooled and thoroughly agitated, and the temperature is watched to see that it does not rise above 22° C. In case of a dangerous rise in temperature, the mixture is run into a tank of cold water. The nitroglycerine, being lighter than the mixed acids and not miscible with them, collects in a layer on top, which is drawn off and purified.

Nitroglycerine is a thick, colorless, odorless liquid, insoluble in water. It solidifies at 4° C., and since the solid is

Robert Kennedy Duncan (1868–1914) was born at Brantford, Ontario. From 1910 to 1914 he was director of the Department of Industrial Research of the University of Pittsburgh, and was the founder of the unique system of coöperation between science and industry in operation at the Mellon Institute of the University of Pittsburgh. He was a man who possessed great literary ability and who narrated the great discoveries of modern physical science in language easily understood by the layman, having a style as fascinating as that of a novelist. He was the author of "The New Knowledge," "The Chemistry of Commerce," and "Some Chemical Problems of To-day."

comparatively inert, it is thawed before being used, an operation accompanied by considerable danger. Nitroglycerine detonates when heated to 257° C., and when subjected to a sudden shock, as by a detonating cap. When it explodes, nitroglycerine instantly decomposes into gaseous products. It contains more than a sufficient quantity of oxygen for its complete combustion.

$$4\ C_3H_5(NO_3)_3 \longrightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$$

When six cubic inches of nitroglycerine explodes, the power exerted is sufficient to lift nine tons to a height of one yard in one forty-thousandth of a second. The quickness of the explosion explains the downward effect that nitroglycerine manifests in shattering rock and earth on which it is placed.

555. Dynamite. — For convenience in use and to vary its explosive power, various porous solids are used to absorb nitroglycerine. Such mixtures are called *dynamite*. A modern dynamite is a mixture of 13% wood pulp, 33% nitroglycerine, and 54% sodium nitrate. The sodium nitrate is used to furnish oxygen for the combustion of the wood pulp. Sometimes the wood pulp itself is partly nitrated.

556. Esters of Organic Acids. — Animal and vegetable oils and fats are esters of glycerine and various organic acids, among the more common of which are palmitic acid, $C_{15}H_{31}COOH$, stearic acid, $C_{17}H_{35}COOH$, and oleic acid, $C_{17}H_{33}COOH$, a monobasic acid of the ethylene series. Glyceryl palmitate is commonly called palmitin; glyceryl stearate, stearin; and glyceryl oleate, olein.

557. Soaps and Soap Making. — *A soap is a metallic salt of a fatty acid*, that is, it is a salt of an acid that may be obtained from a fat or an oil. Common hard soap is a mixture of the sodium salts of stearic, oleic, and palmitic acids. For the purpose of illustration, let us consider hard beef fat to be stearin (glyceryl stearate). When such a fat is boiled with a solution of sodium hydroxide, double replacement takes place, resulting in the formation of a soap (sodium stearate) and glycerine.

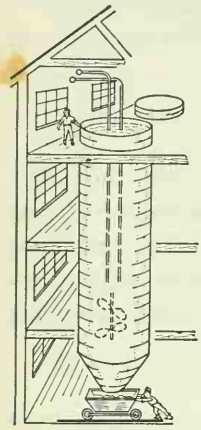


FIGURE 223.

A huge modern soap kettle. Fat and sodium hydroxide are sprayed in at the top; the heating is accomplished by steam coils and by live steam. 500,000 pounds of soap are made in one operation.

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\ NaOH \longrightarrow 3\ Na(C_{17}H_{35}COO) + C_3H_5(OH)_3$$

Most hard soaps used for household purposes are made by boiling a suitable mixture of fats with a solution of sodium hydroxide in huge kettles. The soap kettle, Figure 223, is fitted with two sets of steam pipes; one, a closed coil to supply heat, and the other an open coil to deliver steam through the charge to keep it stirred. Melted fat and part of the quantity of alkali required for complete saponification are run into the kettle and the steam is turned on. The concentration of the alkali is regulated by the kind of fat used. When the mixture has become homogeneous, a more concentrated alkali is added and the boiling continued until a sample shows that the product has the desired consistency. Salt is then added, and the soap, being insoluble in brine, separates. The kettle is allowed to remain quiet for sev-

eral hours and the soap collects on top of the liquid. This liquid is called *spent lye*. It contains glycerine, water, salt, and impurities from the alkali and fat. The spent lye is drained off, the salt and glycerine are separated from it, and the layer of soap is boiled with sufficient alkali to complete the saponification. During this boiling, rosin is sometimes added. Pure rosin soaps have strong cleansing properties, but are too soft and sticky for general use.

The soap when taken from the kettle is often mixed with one or more of various fillers and water softeners, such as sodium carbonate, borax, and sodium silicate. Coloring materials and perfumes may also be added. Soaps that float are made light by having air forced through them while they are in the pasty condition. *Soap powders* consist essentially of hard soap ground with sodium carbonate.

558. Twitchell Process. — The demand for stearic acid by the candle industry, and the difficulty involved in separating glycerine from spent lye led to the saponification of fats by boiling them with water in the presence of a suitable catalyst.

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\ HOH \longrightarrow C_3H_5(OH)_3 + 3\ C_{17}H_{35}COOH$$

Such catalytic agents have been prepared by an American chemist, Ernst Twitchell, and the process in which they are used is named for him. The fatty acids thus obtained form a layer on top of the water in which the glycerine is dissolved, and from which it is easily separated. Soap is made by causing the fatty acids to react with sodium carbonate.

$$2\ C_{17}H_{35}COOH + Na_2CO_3 \longrightarrow 2\ Na(C_{17}H_{35}COO) + H_2O + CO_2\uparrow$$

559. Cleansing Effect of Soap. — The cleansing effects of soaps are believed to be due to their power to emulsify grease, and to their adsorption by dirt, so that the particles become coated with a layer of soap which prevents the dirt from adhering to the article being washed (§ 358).

560. Action of Soap with Hard Waters. — If a water contains in solution substances yielding ions that will combine with the acid radicals of soap to form an insoluble soap the reaction by which the insoluble soap is formed will run to an end. Since insoluble soaps are of no value for cleansing purposes, a water containing compounds that will react with soap to form an insoluble soap is hard to wash with, that is, it is a *hard water*. When a soluble soap, for example sodium stearate, is used with a water containing calcium ions, an insoluble calcium soap, calcium stearate, is formed:

$$2\,Na(C_{18}H_{35}O_2) + CaSO_4 \longrightarrow Ca(C_{18}H_{35}O_2)_2\downarrow + Na_2SO_4$$

The soap is said to be destroyed, as good suds cannot be formed until the calcium ions are removed from solution. This explains why hard water is not desirable for washing purposes. The hardness of water is measured by its soap-destroying power. This is commonly due to the presence of calcium and magnesium ions in the water. Soap does not form suds with salt water because it does not go into solution. Salt water contains a large number of sodium ions and these keep the soap from dissolving.

561. Hydrogenation of Oils. — The demand for edible fats, and for fats suitable for making high grade soaps, would have caused a serious shortage of such materials, if a process had not been developed by which esters containing unsaturated carbon atoms could be made into hard fats. Oleic

acid differs from stearic acid by containing two carbon atoms joined by a double bond. The unsaturated acid, oleic acid, $C_{17}H_{33}COOH$, is changed to the saturated acid, stearic acid, $C_{17}H_{35}COOH$, by treating the former with hydrogen in the presence of a catalyst — finely divided nickel. Olein, $C_3H_5(C_{17}H_{33}COO)_3$, when treated with hydrogen in the presence of a catalyst, is changed to the hard fat, stearin, $C_3H_5(C_{17}H_{35}COO)_3$

$$C_3H_5(C_{17}H_{33}COO)_3 + 3\,H_2 \longrightarrow C_3H_5(C_{17}H_{35}COO)_3$$

In a similar manner, various unsaturated esters are changed to saturated esters. Commercial applications of the hydrogenation of oils and soft fats have resulted in the production of lard substitutes from cotton seed oil, and the production of hard fats essential to the production of hard soaps of desirable quality. Cotton seed oil, peanut oil, soya bean oil, palm oil, cocoanut oil, and fish oil are a few of the oils that have had their commercial value increased by hydrogenation. It is interesting to note that fish oils may be treated and hydrogenized so that the products are free from a fishy odor.

Ethers

The ethers are alkyl oxides, having the general formula

562. Ether. — Ordinary ether, $C_4H_{10}O$, is diethyl oxide, $(C_2H_5)_2O$. It is prepared by treating alcohol with a dehydrating agent, such as sulphuric acid:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

Ether is a volatile, inflammable liquid, boiling at 35° C. It is used as a solvent and as an anæsthetic.

CARBOHYDRATES

A carbohydrate is a compound of carbon, hydrogen, and oxygen, in which there are two atoms of hydrogen for each atom of oxygen.

563. Starch $(C_6H_{10}O_5)_n$ is the final result of a process that takes place in the leaves of plants by the action of chlorophyll and sunlight on carbon dioxide and water. The reaction is an illustration of *photosynthesis*, a chemical building up of a compound brought about by the action of light. From the leaves, the soluble compounds first formed are transported to other parts of the plant and the final product, starch, is stored in roots, tubers, and seeds.

$$6\ CO_2 + 5\ H_2O \longrightarrow C_6H_{10}O_5 + 6\ O_2$$

Commercially, starch is obtained chiefly from corn. The material is crushed in water, and, after the separation of the coarse, fibrous matter, the starch is allowed to settle from a slowly flowing liquid.

Starch granules consist of soluble starch inclosed in a covering of starch-cellulose. On account of this covering, starch granules are not soluble in cold water. They become changed to soluble starch by any process that will rupture their envelope of starch-cellulose. In the preparation of common starch paste, this is accomplished by boiling the starch. By this process the starch is liberated and forms starch paste, a thick colloidal gel (§ 355). The starch producing this colloidal solution is spoken of as *thick-boiling* starch.

A starch that is miscible with cold water is spoken of as a

soluble starch. If starch is heated to over 100° C. in a closed vessel, and the pressure then suddenly released, the starch granules are burst by the sudden expansion of steam within them, and the product thus obtained forms colloidal solutions with cold water. Soluble starches may be prepared by various methods, such as digesting starch with dilute solutions of acids, or by treatment with dilute solutions of caustic alkalies. Such treatment destroys the envelop of the granules and partially hydrolyzes the starch. *Thin-boiling* starch is starch that has been treated so as to reduce its viscosity. It may be prepared by treating starch with very dilute solutions of acids at temperatures too low to burst the starch granules. The shape of the granules is not destroyed, but a slight hydrolysis of the contents of the granules is supposed to take place. Thin-boiling starches are not soluble in cold water.

564. Dextrines are prepared on a large scale by roasting starch at temperatures ranging from 170° C. to 270° C. Other varieties of dextrine are made by moistening the starch with very dilute solutions of acids preparatory to the heating, which is carried on at even lower temperatures. The dextrines are miscible with water. They are used in large quantities in the adhesive used for envelopes and postage stamps, and also in the textile industries.

Dextrines are not definite chemical compounds. During the process of baking, the starch in the outer portions of a loaf of bread is partially changed to dextrine, which is an important constituent of the crust of the loaf. Starch is also changed to dextrine when bread is toasted. The dextrine thus formed is a valuable food, more easily digested than starch.

565. Cellulose. — The cell walls of plants are composed of cellulose, a compound having a percentage composition corresponding to the formula $C_6H_{10}O_5$. Absorbent cotton and the better grades of filter paper are nearly pure cellulose. It is the chief constituent of straw and wood.

When boiled with acids, cellulose is slowly converted into a sugar called *glucose*. Cellulose dissolves without change in an ammoniacal solution of cupric hydroxide, known as Schweitzer's reagent. The cellulose can be precipitated from such a solution by the addition of alcohol. Concentrated solutions of sodium hydroxide convert cellulose into soda cellulose. This, when treated with carbon disulphide, yields viscose, a substance readily soluble in water. Cuprammonium solutions of cellulose and also viscose are used in the manufacture of artificial silks, which, since the finished product consists of cellulose, are more properly called luster celluloses. Cellulose is dissolved in zinc chloride in making the carbon filaments for the older form of incandescent electric light bulbs. Acetic anhydride is used to convert cellulose into cellulose acetate, a substance useful in the manufacture of electric insulators and moving picture films.

566. Nitrocellulose (*cellulose nitrate*). — When pure, dry cellulose is treated with a cold, concentrated mixture of nitric and sulphuric acids, a substance called nitrocellulose is formed by an action analogous to that used in the making of nitroglycerine. A part or all of the hydroxyl groups in the cellulose are replaced by a corresponding number of NO_3 groups. The number of NO_3 groups introduced varies with a number of factors, such as the composition of the acid mixture, the temperature under which the nitration takes place,

and the length of time the cellulose remains in contact with the acid mixture.

By varying the conditions under which the nitration takes place, nitrocelluloses having different properties can be made. Nitrocelluloses containing 13% and over of nitrogen are insoluble in a mixture of two volumes of ether with one volume of alcohol, and constitute true guncotton. Nitrocelluloses containing a less percentage of nitrogen are soluble in the ether-alcohol mixture. They are called *pyroxylin*, or collodion cotton. *Collodion* is a solution of pyroxylin in a mixture of alcohol and ether.

Collodion, celluloid and allied substances, certain classes of smokeless powders, zapon varnish and lacquer are a few of the substances produced by the great nitrocellulose industries.

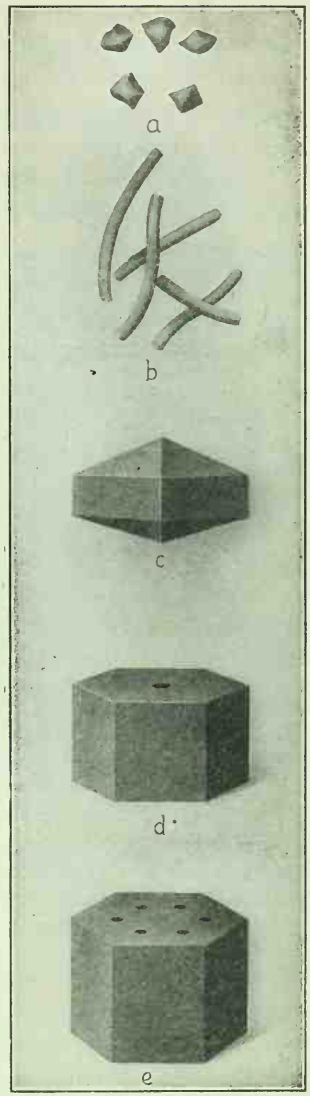


FIGURE 224.

Important explosives: *a* is granular gunpowder; *b*, cordite; *c*, giant powder; *d*, brown, prismatic powder; *e*, maximite. All explosives contain unstable nitrogen compounds.

Celluloid is made by incorporating camphor with pyroxylin. *Blasting gelatin*, or gelatin dynamite, is made by dissolving one part of pyroxylin in nine parts of nitroglycerine. The product is a clear, jelly-like material, extensively used for blasting. It is the parent of modern smokeless powders.

A great variety of smokeless powders are made from the nitrocelluloses, or from mixtures of nitrocellulose with one or more of a great variety of substances.

Cordite (Fig. 224) is a smokeless powder made by incorporating guncotton with nitroglycerine by use of a common solvent, acetone. A small quantity of vaseline is added to the mixture to prevent corrosion of the gun. On evaporation of the acetone, the solid cordite remains.

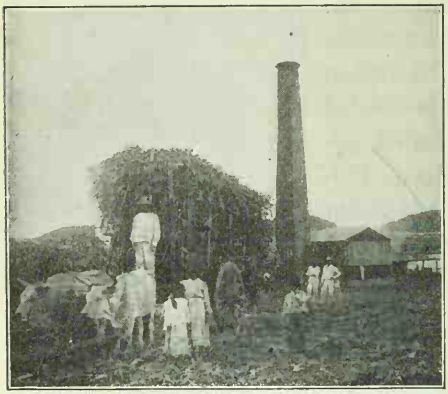


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FIGURE 225.

Sugar making in Cuba. Oxen carry great loads of sugar cane to the mill, where it is crushed and the resulting juice evaporated; a crude sugar is thus produced.

567. Sugars. — A very large number of sugars are known. *Levulose*, or fruit sugar; *dextrose*, or grape sugar; and *saccharose*, or cane sugar, — are among the more important. Levulose and dextrose have the empirical formula $C_6H_{12}O_6$; the formula for saccharose is $C_{12}H_{22}O_{11}$.

Dextrose, $C_6H_{12}O_6$. — Enormous quantities of corn starch are hydrolyzed to dextrose and intermediary products.

The hydrolysis is brought about by cooking the starch under pressure in water acidulated with about one tenth of one per cent of hydrochloric acid.

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

Glucose is scientifically another name for dextrose, but commercially the name glucose has been applied to corn sirup, a mixture of glucose with compounds such as dextrine and maltose produced by the incomplete hydrolysis of starch.

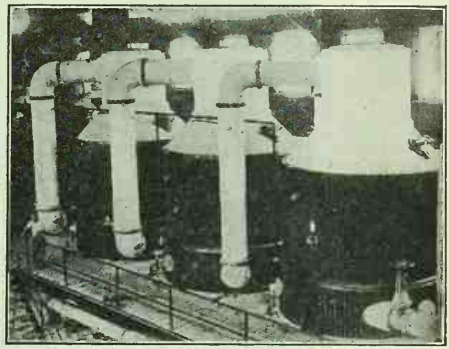

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FIGURE 226.

Great vacuum pans are used in boiling down sugar solutions in the process of refining crude sugar. They permit of the use of a lower temperature, and lessen loss that would otherwise result from overheating the sugar.

Dextrose is converted by a ferment (zymase) secreted by the yeast plant into alcohol and carbon dioxide:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2\uparrow$$

This fermentation is made use of in the raising of bread and in the preparation of alcohol. It also is the cause of the formation of hard cider.

Large quantities of glucose are used in making candies and table sirups.

Saccharose is converted into dextrose and levulose by boiling with water:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Dextrose and levulose have the same empirical formula.

Dilute acids hasten this action, which is known as inversion. For this reason vinegar is often added to sugar during the making of candy that is to be pulled.

Zymase does not convert saccharose into alcohol and carbon dioxide. However, the yeast plant secretes another

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FIGURE 227.

Sugar making in Vermont. The sap of the sugar maple is caught in buckets. Not all of the sap will reach the sap house in this case.

ferment called *invertase*, which changes saccharose to a mixture of dextrose and levulose. These, as has already been mentioned, can be fermented by zymase.

Common sugar melts at 160° C. to a colorless liquid which solidifies on sudden cooling to a transparent amber-colored mass, called *barley sugar*. When sugar is heated

to 215° C., some water is expelled and a brown mass, *caramel,* is obtained.

568. Sugar Manufacture and Refining. — Sugar is obtained from the juices of the sugar cane and beets and from

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FIGURE 228.

Sugar making in Vermont A view in the sap house, where the sap of the maple tree is efficiently evaporated in a long shallow pan over a wood fire. As the sap thickens, it travels in the direction of the flames to less intensely heated parts of the pan.

maple sap. After extraction, slaked lime is added to the juice to prevent fermentation and to precipitate the albuminous substances coming from the plant cells. The solution is then filtered through cloth and evaporated in a vacuum pan at a temperature of about 66° C. If the evaporation

were carried on under ordinary pressure, the temperature would become sufficiently high to invert the sugar.

As soon as a sample taken from the vacuum pan shows that sugar will crystallize when the sirup cools, the solution is removed from the pan and allowed to cool. The

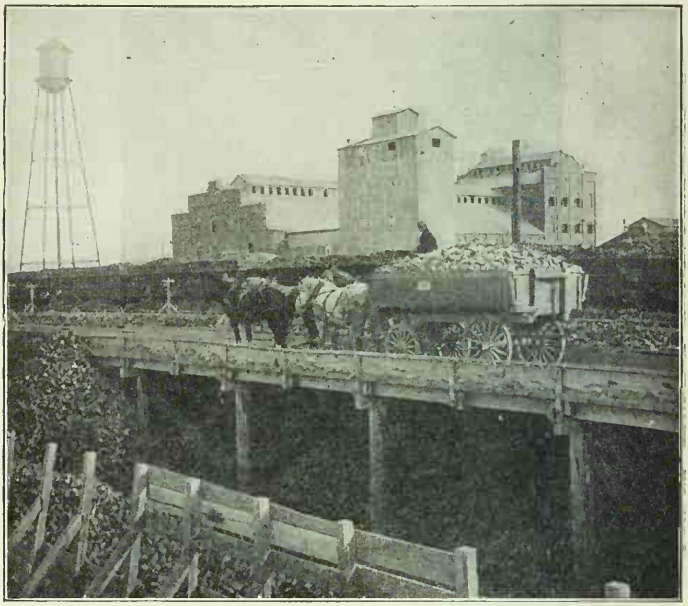

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FIGURE 229.

Sugar making in Nebraska. These beets were grown in the Bad Lands of Nebraska, formerly regarded as useless for agriculture.

crystals are dried in centrifugal machines. The product obtained is usually raw sugar, which must be refined before being placed on the market. Nearly all sugar refineries are in the northern states.

The raw sugar is dissolved in large vats and the sirup

pumped to the top of high buildings, where it is mixed with lime and a little monocalcium phosphate to coagulate any albuminous material or other colloid, that may have been left in the sugar. The sirup is then filtered to remove the coarse impurities that are suspended in the solution. After this, the liquid is filtered through boneblack to remove the coloring matter. The purified sirup is boiled in vacuum pans as in the case of raw sugar.

SUMMARY

A **structural formula** represents the arrangement of the atoms in a molecule.

A **hydrocarbon** is a compound composed of carbon and hydrogen.

A **saturated** carbon compound contains no two carbon atoms united by more than one bond.

An **unsaturated** carbon compound contains at least two carbon atoms united by more than one bond.

The **methane** series of hydrocarbons is a saturated series. It has the general formula C_nH_{2n+2}, in which n stands for the number of carbon atoms in the compound. Each member of the series differs from the preceding member by CH_2.

Isomers are compounds having the same percentage composition, but possessing different properties on account of differences in the arrangements of the atoms in the molecule.

The **ethylene series** is an unsaturated series having the general formula C_nH_{2n}.

The **acetylene series** has the general formula C_nH_{2n-2}.

The **benzene series** has the general formula C_nH_{2n-6}.

Methane, acetylene, benzene, and toluene are important hydrocarbons.

A **halogen substitution product** is considered as derived from a hydrocarbon by the exchange of one or more hydrogen atoms for

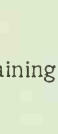
a corresponding number of halogen atoms. Chloroform and carbon tetrachloride are examples of substitution products.

An **alcohol** may be considered as derived from a hydrocarbon by exchanging one or more hydrogen atoms for a corresponding number of hydroxyl groups. Two hydroxyl groups seldom remain attached to the same carbon atom.

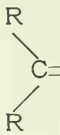
Methyl alcohol, ethyl alcohol, and glycerine are important alcohols.

Ethyl alcohol is made by the action of an enzyme, zymase, on a fermentable sugar such as dextrose. Alcohol is separated from the fermented liquid by fractional distillation.

Denatured alcohol is ethyl alcohol mixed with other substances to produce a poisonous solution having a disagreeable odor. There is no internal revenue tax on denatured alcohol.

An **aldehyde** is a carbon compound containing the group  .

Formic aldehyde is made by the partial oxidation of methyl alcohol.

A **ketone** is a carbon compound having the general formula  . Acetone is an important ketone.

An **organic acid** contains one or more carboxyl (COOH) groups.

An **ester** is the product other than water formed when an acid reacts with an alcohol, the alcohol playing the part of a base. Animal and vegetable fats and oils are esters of glycerine and various organic acids. Nitroglycerine is an ester. It is easily decomposed and contains more than sufficient oxygen for its complete combustion. The products of combustion are all gases at the temperature of the explosion.

A **soap** is a metallic salt of a fatty acid. Ordinary soaps are

essentially the sodium soaps of palmitic, oleic, and stearic acids. Fatty acids may be obtained from fats by boiling the fat with water in the presence of a catalytic agent. (Twitchell Process.)

A **hard water** contains in solution substances that react with soap to form an insoluble soap.

The **hydrogenation of oils** is brought about by the use of a catalytic agent to cause oils containing unsaturated compounds to combine with hydrogen to form saturated compounds.

Ethers are alkyl oxides. Sulphuric (ordinary) ether has the formula $(C_2H_5)_2O$.

A **carbohydrate** is a compound of carbon, hydrogen, and oxygen, in which there are two atoms of hydrogen for each atom of oxygen.

Cellulose, starch, dextrose, levulose, and saccharose (cane sugar) are important carbohydrates.

Dextrose is made by boiling starch with water acidulated with hydrochloric acid.

Dextrines are prepared by roasting starch at temperatures between 170° C. and 270° C.

The **nitrocelluloses** are cellulose nitrates.

EXERCISES

1. Why is it frequently desirable to use the structural formula of an organic compound?

2. What is a hydrocarbon?

3. A hydrocarbon of the methane series contains three carbon atoms. Give its structural formula.

4. How many pentanes (C_5H_{12}) are possible? Write their structural formulas.

5. What is the structural formula for acetylene?

6. Why is carbon tetrachloride preferable to gasoline for home use in the removal of grease spots from clothing?

7. Define alcoholic fermentation; acetic fermentation.

8. What is an alcohol?

9. Give the formulas for three common alcohols.

10. What is denatured alcohol? Why is alcohol denatured?

11. What group of elements is characteristic of aldehydes?

12. What relation does formaldehyde bear to wood alcohol?

13. To what class of organic compounds does acetone belong?

14. What is Prest-O-Lite?

15. What group of elements is characteristic of organic acids?

16. What relation does acetic acid bear to alcohol?

17. What important chemical changes take place when sweet cider changes to vinegar?

18. To what class of compounds do animal and vegetable fats belong?

19. Why is it possible to hydrogenate olein and not possible to hydrogenate stearin?

20. Why is the hydrogenation of oils of great economic importance?

21. What is nitroglycerine? Dynamite?

22. How is soap made?

23. What are the principal constituents of soap powders?

24. What reaction takes place when soap is added to a water containing magnesium sulphate? Why?

25. Why do not soap suds form readily when soap is added to salt water?

26. Name three common carbohydrates.

27. Why is not boiling water used to prepare starch from corn?

28. Name a solvent for cellulose.

29. How is dextrine obtained from starch?

30. Would you expect to find dextrine in the crust or in the center of a loaf of bread?

31. What substance is used to remove the coloring matter from crude sugar?

32. Why are sugar solutions boiled in vacuum pans?

33. Why is vinegar used in making sugar candy that is to be pulled?

34. What is barley sugar? Caramel?

35. Name five organic substances used in the home and mention a natural source of each.

36. Write the chemical equations for:

(*a*) the making of formaldehyde from wood alcohol;
(*b*) the acetic acid fermentation of alcohol;
(*c*) the making of nitroglycerine;
(*d*) the reaction between alcohol and acetic acid;
(*e*) the manufacture of a hard soap.

37. What is meant by the *inversion* of cane sugar?

38. Give two equations that show the two steps in the conversion of cane sugar into alcohol.

CHAPTER XXXIX

RADIUM AND RADIOACTIVITY

569. The Discovery of Radioactivity. — In 1896 the French chemist Becquerel, while investigating the penetrating powers of the rays emitted by phosphorescent substances, happened to leave a compound of the element uranium spread out on the thick paper that inclosed a photographic plate. At the end of four weeks it was found that the plate had been affected by rays which had issued from the uranium compound, and which had penetrated the thick paper that inclosed the plate. Investigation showed that the result was in no way connected with the phosphorescent properties of the substance, since identical effects were observed whether the uranium compound was in the phosphorescent state or not. It appeared that the substance *continuously* gave off rays which produced photographic and electrical effects without being itself changed in the process.

This half-accidental discovery of Becquerel's led to investigations which have marked an important era in the history of chemistry. The term *radioactivity* was given to effects like those produced by uranium compounds.

570. The Discovery of Radium. — Madame Curie, a Polish woman resident in Paris, took up a series of researches along the line indicated by Becquerel's discovery. She found that all uranium compounds possess radioactivity,

Marie Slodowska Curie was born in Warsaw, Poland, in 1867. Her work began with the investigation of radio-activity first noticed by Becquerel in connection with uranium. She first isolated polonium, an element possessed of radio-activity in high degree, and later, in collaboration with her husband, Pierre Curie, made the epoch-making discovery of radium. For this work they received the Davy Medal of the British Royal Society, and shared with Becquerel, in 1903, the award of the Nobel Prize in Physics. Madame Curie succeeded her husband as the holder of one of the most important chairs of science in the world, the Professorship of Physics at the Sorbonne, University of Paris.

and hence that this is a property of the uranium *atom*. She then observed that pitchblende, the mineral from which uranium is usually obtained, is more radioactive than might be expected from the amount of uranium present. She reasoned that the mineral must, therefore, contain something more active than uranium. Working with this point in view, she found that bismuth and barium *when extracted from pitchblende* are radioactive. But ordinary bismuth and barium are not radioactive. Hence it was probable that when extracted from pitchblende the two metals contained small quantities of other elements, chemically similar to themselves, and radioactive in a high degree. Madame Curie set out to find these elements.

She was soon able to show that bismuth obtained from pitchblende is in reality associated with an element many times more active than uranium. This element was named *polonium* in honor of her native country.

Her next work resulted in what probably always will be regarded as one of the greatest of chemical discoveries. This was the separation of a minute quantity of the element that is associated with pitchblende barium. It was named *radium* because of the extraordinary degree of radioactivity that it exhibited. The study of this remarkable substance has led to a better understanding of the nature of atoms, and to important changes in chemical theories.

571. The Nature of Radioactivity. — The peculiar characteristics possessed by radioactive bodies are due to emanations or radiations that they produce. Three types of such emissions have been recognized. They are designated by three Greek letters, α (alpha), β (beta), and γ (gamma). Of these, the α and β emanations have played the most impor-

tant part in radium investigations. The original basis of the classification of the three types of rays was their penetrating power. The α type has the least power, though these rays will pass through a sheet of paper or even through very thin glass. The β particles have, roughly speaking, 100 times the penetrating power of the α type, and the γ rays have about 10,000 times the power of the α. These γ rays will traverse a foot of solid iron or six inches of the dense metal lead. They are identical with X-rays discovered by Roentgen. The β particles consist of minute particles of negative electricity (electrons).

The α radiation has been shown to be *atoms of the element helium* positively electrified. Helium has been recognized as an element for many years. It was first discovered by the aid of the spectroscope as a constituent of the gases that surround the sun (§ 241). A few years before the radium investigations it was found as one of the rare gases of the atmosphere. Thus through radium we have found an actual case of the transmutation of elements, and, in a sense, the old, laughed-at idea of the alchemists has been revived in the mind of chemists.

Another extraordinary thing about radium is that it is continually giving off energy through its emanations. When a bit of radium is placed beside the bulb of a thermometer and the two are wrapped in a bit of cotton or wool, the thermometer stands a degree or two higher than the temperature of the room. But so far as ordinary observation reveals, the substance is absolutely unchanged either in properties or weight. Here we have an apparent contradiction of the law of the conservation of energy. Another and more striking experiment showing the continuous emission of energy is found in the *radium clock* (Fig. 230). A

small quantity of radium bromide is contained in a metal tube from which are suspended two pieces of gold leaf. The leaves separate, owing to the fact that they are electrically charged by the negative electricity or the charged particles that are shot off by the decomposing radium atoms of the radium. On diverging, the leaves touch the strips of metal on the inside of the bottle which contains the apparatus and discharge their electricity. They then fall together, are again charged by the radium, and again separate. Since the radium compound does not apparently diminish in producing this action, the clock will seemingly go on forever. In other words, we have realized a sort of perpetual motion.

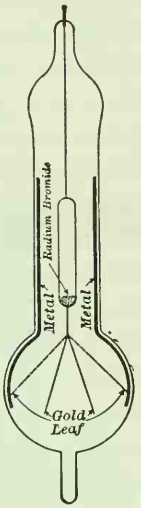


FIGURE 230. The radium clock seems to have perpetual motion. Its energy, however, comes from the decomposition of the radium atoms.

These three examples will serve to show how radium seemed to upset established physical and chemical ideas. It remains for us to show how these things were explained by an extension of older ideas.

572. Radioactive Decay. — Let us consider further experimental facts. Radium is always found in ores that contain uranium, in the definite proportion of 1 part of radium for about 3,200,000 parts of uranium. Radium compounds when recrystallized from water solution are found to be inactive, but regain their activity on standing a few days. The water which is used in the process gives off a minute quantity of a radioactive gas. This rapidly loses its activity, so that in little more than five days it is only one half as active as before. Objects that come in contact with

this gas, or that have been near radium, become active; but if these objects are rubbed with sandpaper, the activity is found to be attached to the scraping material; this acquired activity, however, decays to half its value in about thirty minutes.

The study of the duration of radioactivity is carried out with the aid of the *electroscope* (Fig. 231), an apparatus that is somewhat similar in construction to the radio clock described above. Two leaves of gold foil are suspended from a metal rod. When charged with electricity, the two leaves fly apart. They will ordinarily remain apart for some time, since air is a poor conductor and there is no chance for the electricity to escape. But in the presence of radium emanations, the molecules of air become charged and hence capable of conducting electricity away from charged objects. It thus happens that the charged leaves of an electroscope will fall together in the presence of radioactive emanations. This instrument is far more sensitive in revealing minute quantities than any other known to chemists. By its use, the degree of activity of radioactive materials can be measured.

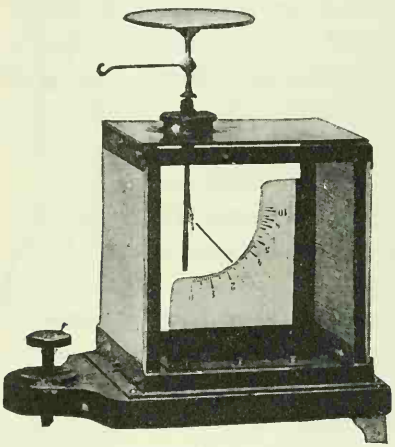


FIGURE 231.

An electroscope. Beside the vertical bar hangs a strip of gold leaf. When a charged object is put on the plate the rod and leaf acquire the same sort of charge, and the leaf is repelled from the rod. This instrument is the chief means of revealing the presence of radioactive substances.

573. Radioactive Series. — In adopting these new explanations it was found necessary to abandon the old idea that an atom is an unchangeable thing. It is now believed that radioactive elements are continuously undergoing processes of decomposition. During the changes, two important things occur: (*a*) relatively *enormous amounts of energy* are liberated, and (*b*) new elements are produced. It appears that certain of the atoms explode from time to time, producing the various radioactive effects. Sometimes it is a helium atom that is thrown off, sometimes a β emanation, and at other times the loss of both occurs. In each case, the greater part of the exploding atom remains intact and forms the atom of a new element. This explodes in its turn, and thus we have a series of radioactive elements resulting from one parent element. Since helium has an atomic weight of 4, the loss of an α emanation produces a new element whose atomic weight is less by 4 than that of the parent atom. The β emanation apparently produces no effect on the atomic weight.

Two main series of such radioactive transformation have been recognized. Uranium is the parent element in one series, and thorium in the other.

574. The Uranium Series. — Different radioactive elements vary greatly in the speeds with which they decompose. The less active ones decompose slowly, the more active rapidly. Thus, in the case of uranium, which is very slightly active, it has been calculated that it would take 8,000,000,000 years for half of the atoms in a given mass to change into other substances. It would take another 8,000,000,000 years for half of the remainder to decompose, and so on. The "life" or period of one of these elements is measured by the time it would take for half of its atoms to change.

The uranium atom, atomic weight 238, in decomposing, produces an atom of helium, atomic weight 4, and an atom of uranium X_1, atomic weight 234, period 35.5 days. The next transformation involves the loss of a β particle and results in uranium X_2, period 1.65 minutes, atomic weight also 234. Then another β emanation is given off, producing uranium 2, period 30,000,000 years, atomic weight, as before, 234. Next a helium particle is expelled, resulting in ionium, atomic weight 230, period 2,000,000 years. The next decomposition takes place with the loss of another helium atom, and *radium*, atomic weight 226, period 2440 years, results. One reason that this element has played the most important part in radioactive investigations is that its period is long enough to permit study, and at the same time short enough to give the element a high degree of activity.

Radium atoms in their explosions give off helium atoms and a new element described above as the gas obtained from solutions of radium salts. This is an extremely active substance, whose period is 5.55 days, identified by Ramsay as niton, now called radon. It can be obtained only in very minute quantities, but by means of a balance of extreme sensibility it was weighed and its atomic weight found to be 222. This is what we would expect to result from radium by loss of a helium atom. Radon in turn decomposes and successive short-lived elements are produced until finally an end-product element of atomic weight 206 is reached. This is very close to the atomic weight of lead, and it is believed that this element is produced as the final result of the series of uranium decompositions. Thus the radium that is formed in pitchblende resulted from the decomposition of uranium; and since radium itself decomposes, we can never expect to find more than a minute quantity of radium in any ore.

575. Thorium Series. — Thorium is a comparatively rare element whose oxide is used as the chief constituent of gas mantles. It is a radioactive substance of very long period. Its minerals always contain small quantities of its decomposition products, some of which are as active as radium and are even more important as commercial sources of radioactive material.

576. The Structure of Atoms. — Since radioactivity is due to the decomposition of atoms, it is apparent that these must be complex, not simple, in structure. Chemists now believe that all atoms are composed of positive and negative electricity; the positive part of the atom is supposed to be concentrated in a nucleus, which is small in comparison with the size of the atom itself; the negative electricity consists of the β particles, called electrons, which we have described as being given off in radioactive decomposition. The electrons are arranged about the central positive nucleus, at a considerable relative distance from it, and are possibly in a state of rotation. The weight of an atom is almost wholly due to the positive nucleus.

Investigations now in progress on this matter are in process of explaining much that was not understood concerning the periodic system. It is certain that the properties of the elements are determined partly by the number and partly by the arrangement of the electrons. We may have elements having the same chemical properties, but possessed of different atomic weights. Such similar elements are called *isotopes*. As an example, lead derived from ores that contain thorium but no uranium has an atomic weight different from the lead that is obtained from ores that contain uranium but no thorium. We may also have elements that have identical

atomic weights, but very different chemical properties. Such elements are called *isobares*. It has been suggested that ferrous and ferric iron are isobares.

577. Chemical Action and Valence Explained. — Tendencies to chemical action are due to tendencies of atoms either to gain or to lose electrons. An element which has a tendency to lose electrons combines chemically with one that has a tendency to gain electrons. A univalent positive element, like sodium, is one that readily loses one electron, and thus remains positively charged. A univalent negative element, like chlorine, is an element that readily takes on another electron and thus becomes negatively charged. Divalent elements either readily lose two, or gain two electrons.

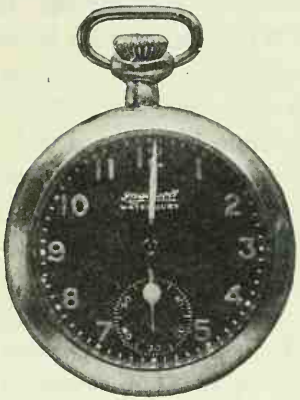


FIGURE 232.

Although the price of radium is stated in terms of tens of thousands of dollars per fraction of a gram, yet it is so extraordinarily active that a few cents' worth suffices to make luminous the figures and hands of clocks and watches.

578. The Value of the Radium Discoveries. — On the discovery of radium, investigations were at once started in the hope that its extraordinary radiations might act as a cure for cancer. In certain forms of the disease, the emanations have proved of great value. As sources of energy the radioactive substances are truly remarkable. A bit of radium in changing down to lead gives out 300,000 times as much energy as does an equal weight of coal in burning. It has been observed

that if chemists ever succeeded in producing gold from the atomic decomposition of elements of higher atomic weight, the energy liberated might be comparable in value to that of the gold itself. The explosions of radioactive atoms are due to spontaneous rearrangements of the electrons within the atom. It is believed that the atoms of all elements might undergo radioactive transformation if we could find a method of causing them to take place; and that the transmutations of elements are within the range of final possibility. According to this point of view, there is an inexhaustible amount of energy stored up in atoms, and it is conceivable that some day this may be made available. It will be necessary to find a way of inducing the transformations to take place, just as it was necessary for some one to find how to build fires to make the energy of fuels available. It is possible that all atoms are actually undergoing decomposition continuously, but at such slow rate that we are not able to observe the process.

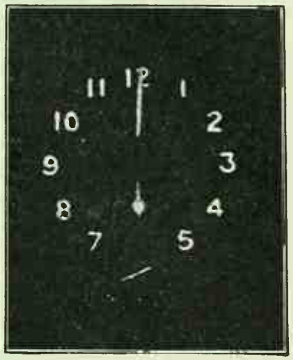


FIGURE 233.

How the watch looks in the dark. The material used in painting the figures is zinc sulphide that contains a minute quantity of a radium compound.

By exposing zinc sulphide to radioactive emanations, or by mixing it with minute quantities of radioactive substances, a paint is obtained which will be luminous in the dark. This is used as a pigment for the figures and hands of watches (Fig. 233) and clocks, and as a surface coating of electric push buttons.

The young student is likely to wonder why so much importance is attached to a thing of theoretical interest like radium. It appears to him that a substance of which there are only two or three grams in the world, and whose market value is something like $1,800,000 per ounce, cannot be of much real use. But in taking this point of view he forgets two things. The first is that, in the main, practical discoveries and inventions follow theoretical development. The second is that there is, in the human mind, a need for understanding the things that are about us, and that this need is a more permanent part of human nature than even the desire for material progress. It is this latter need that the radioactive discoveries have satisfied in such high degree.

SUMMARY

Radioactivity is a name given to an action by which certain elements give off continuously large amounts of energy without undergoing chemical action.

The energy is given off in the form of rays or radiations which produce electrical and other effects. Three types of these rays are recognized, known respectively as the **α, β, and γ radiations.** They all have the power to penetrate solid substances, that of the α variety being very slight, that of the β somewhat greater, and that of the γ very great.

The cause of radioactivity is a **decomposition of the atoms** of **radium** and other radioactive elements that produce the effect.

The remaining mass consists of atoms of another element. The **α radiation** consists of positively charged helium atoms. This fact constitutes a case of transmutation of elements.

The **β radiation** consists of particles of negative electricity, which are called **electrons.** The **γ radiations** are x-rays.

Since a radioactive element gradually decomposes, it follows that such elements have a definite life period. This is usually stated as

the "**half life**," meaning the time it would take for half of the atoms in a given quantity to decompose. This period is 2500 years for radium. That of some of the elements is only a few seconds, that of others is millions of years. The shorter the period, the greater the degree of radioactivity.

Two series of radioactive elements have been recognized. **Uranium**, the "parent" element in one series, by successive losses of radiation (including frequently, but not always, the α type helium atoms), passes into elements of lower and lower atomic weight. Radium and polonium are included in this series. Lead is believed to be the end of this series of decompositions.

A thorium series has also been recognized.

The radium discoveries are regarded as important chiefly because they have brought about **changes in important chemical theories**. We now believe that atoms of all elements are composed of positive nuclei, surrounded by particles of negative electricity, called **electrons**. The β radiation consists of these particles.

Radioactive elements are used in the treatment of cancer and in the manufacture of luminous pigments.

EXERCISES

1. Why was the isolation of radium from pitchblende regarded as a brilliant piece of chemical work?

2. In what respects does radium differ strikingly from ordinary elements? In what respects does it resemble them?

3. Is it true that we could produce perpetual motion by means of radium? Explain.

4. Distinguish between the α, β, and γ radiations emitted by radioactive elements.

5. Why is thorium classed as a radioactive element?

6. What is meant by the period of a radioactive element?

7. What means would you use to test a mineral for the presence of radioactive elements?

8. What relation is there between the period of a radioactive element and its degree of activity?

9. Explain how radioactivity has given a new conception of the character of atoms in general. Describe the modern theory of the structure of atoms.

10. What is meant by saying that enormous amounts of energy are liberated by radioaction?

11. What ancient idea of the alchemists has been revived by the radium discoveries?

12. Name a radioactive element of very short period; one of very long period.

13. For what reasons is the price of radium very great?

14. What new conception of valence has resulted from the electron theory of atoms?

15. Why is radium always found in ores that contain uranium?

16. Why can we never expect to find radium in more than a very small amount in any mineral?

17. Explain how the luminous figures and hands of a watch are produced.

18. Describe the accidental but important discovery made by Becquerel in 1896.

19. Give three facts relating to the recognition or discovery of helium as an element.

20. How may radioactive substances be recognized?

21. What is the evidence that radioactive materials are constantly losing energy?

22. Describe the radium clock. Explain its action.

23. Explain what is meant by radioactive decay.

24. State the steps in the progressive radioactive decomposition of uranium by which a series of elements is obtained resulting finally in radium.

25. If a piece of gas mantle is left on a plate-holder containing a photographic plate, the pattern of the mantle appears on the plate when it is developed. Explain.

CHAPTER XL

GASES AND THEIR MEASUREMENT

579. Gas Pressure. — The peculiar properties of gases are due to the fact that the particles composing them are at considerable distances from each other and are in rapid motion. As these particles pelt against the walls of the containing vessel, they exert a pressure on the walls. If a gas is compressed into a smaller space, more particles will strike a square inch in a given time, and so the pressure measured in pounds per square inch will increase. The increasing pressure of the air in a bicycle pump as the piston is forced down illustrates this. If a gas is heated without being allowed to expand, its pressure on the walls of the vessel containing it will be increased, because the heat increases the speed of the particles of the gas.

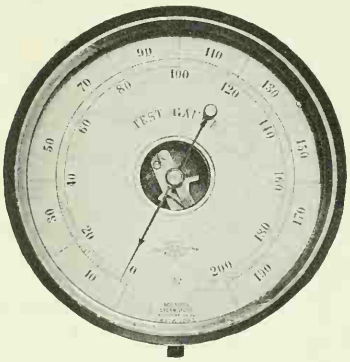


FIGURE 234.
A device for measuring the pressure of gases.

The air that surrounds us is compressed by the weight of the atmosphere above it. The pressure due to the weight of the atmosphere is about 15 pounds per square inch at sea

level and is less at higher altitudes. It is not, however, a constant quantity, but varies with weather conditions. While the pressure of confined gases, like steam or compressed air, is measured by a pressure gauge (Fig. 234), atmospheric pressure is measured by the height of the column of mercury that it supports in a barometer (Fig. 235).

The barometer consists of a tube that has been entirely filled with mercury and then inverted into a reservoir of the same liquid. A pressure of 14.7 pounds per square inch is equal to the weight of a column of mercury 1 in. square, and 30 in. or 760 mm. high. As the gases whose volume we measure in the laboratory are usually subject to atmospheric pressure, gas pressures in chemical work are generally expressed in *millimeters of mercury* instead of pounds per square inch.

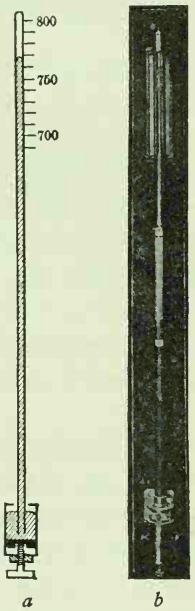


Fig. 235. — Barometer.

a, Section; *b*, External view. A barometer consists of a tube more than thirty inches long. Mercury fills the greater part of the tube; above is a vacuum. The column of mercury balances the weight of the air, the length of the column thus serves as a measure of atmospheric pressure.

580. Effect of Temperature and Pressure Changes on Volumes of Gases. — The measurement of the volume of gases usually involves *a correction of the gas volume.* This is necessary because the volume of a given quantity of gas is considerably affected by even slight changes in temperature and pressure. If the room gets warmer, the volume of the gas

will be larger; if it gets colder, the volume will be less. Changes in atmospheric pressure will also cause the volume to vary. An increased pressure will mean a diminished volume, and a decreased pressure an increased volume.

The measurement of gases in experiments like the analysis of air will be of little value unless account is taken of the temperature and pressure changes. For this reason it becomes necessary to know to what extent these affect the volumes. This is not a difficult matter, for it is found that all gases contract or expand in almost exactly the same degree when they are subjected to the same changes. This regularity is somewhat surprising. A similar thing is not at all true for solids or liquids. Any observed regularity of this sort is called a *law*.

581. Charles' Law. — It is found that if a certain quantity of any gas is made to have a temperature of 0° C., and then is warmed one degree, the gas expands $\frac{1}{273}$ of its volume. Warmed to 10°, it expands $\frac{10}{273}$ of its volume. Heated to 273°, its volume will be doubled. On cooling the gas, we find that it contracts $\frac{1}{273}$ *of its volume at 0° C.* for each degree below 0° C. At −273° C. the volume of the gas would be zero, *if contraction continued at the same rate.* As a matter of fact, all known gases become liquids before this temperature is reached.

This point, −273° C., has been selected as the zero of another temperature scale known as *absolute temperature* (Fig. 236). Since the size of the absolute degree is the same as the Centigrade degree, and since the absolute zero is 273 degrees below the Centigrade zero, a Centigrade temperature is changed to an absolute temperature by adding

it, algebraically, to 273. Thus, 24° C. becomes 297° absolute (273 + 24); −12° C. becomes 261° absolute (273 − 12).

The general statement of the relation between the volume of a gas and its temperature is known as *Charles' Law*. Charles' Law may be stated thus:

If the pressure does not change, the volume of a gas varies directly as the absolute temperature.

582. Use of Charles' Law in correcting Gas Volumes. — By using this law we can calculate the volume of a gas at a temperature differing from that under which it is measured. For example, a quantity of air measures 25.6 c.c. at a temperature of 21° C. Find its volume at 0° C.

$$21° \text{ C.} = 294° \text{ abs.}$$
$$0° \text{ C.} = 273°.$$

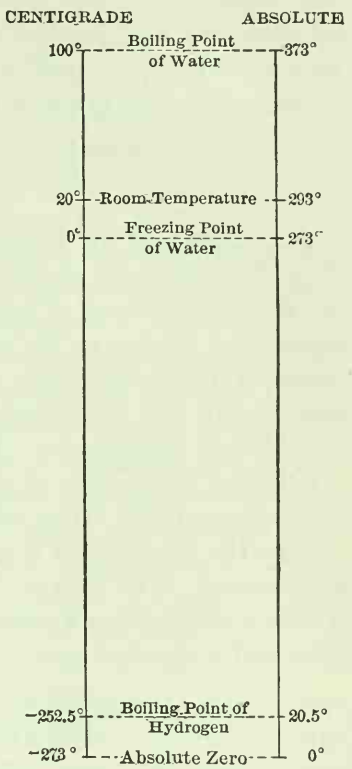


FIGURE 236. — CENTIGRADE AND ABSOLUTE TEMPERATURE SCALES.

Centigrade temperatures are changed into absolute temperatures by adding 273.

The two absolute temperatures 294° and 273° are the real measures of the change in volume. The new volume will be found by multiplying the original volume by a fraction expressing the ratio between these two numbers. If

the temperature were actually changed from 294° to 273°, the gas would be cooled and would contract. The volume at 273° would be less than the original volume. The fraction by which we multiply the original volume will, therefore, have the smaller number for the numerator, and the new volume will be $\frac{273}{294}$ of the original volume. Hence:

$$v = 25.6 \text{ c.c.} \times \frac{273}{294}$$
$$= 23.7 \text{ c.c.}$$

583. Correction for Temperature. — The temperature of 0° C. (273° abs.) is chosen as the standard temperature for the measurement of gas volumes. The operation of finding the volume at the standard temperature is called *correcting* the volume *for temperature.* Sometimes it is necessary to find the volume at a temperature other than the standard temperature. The operation is a similar one.

Example: A quantity of gas has a volume of 75 c.c. at a temperature of 24°. What will be its volume at 100°?

Since the temperature is increased, the volume will also be increased. The fraction by which the original volume is to be multiplied has a numerator greater than the denominator and is therefore greater than one.

$$v = 75 \text{ c.c.} \times \frac{373}{297}$$
$$= 94.2 \text{ c.c.}$$

584. Boyle's Law. — Experiment shows that if the pressure on any gas is doubled and the temperature kept constant, the resulting volume will be one half the original volume. Under a pressure three times as great, the volume is one third. If the pressure is made one third the original pressure, the volume will become three times the original volume. In general, the greater the pressure, the less the

volume in a proportional degree. This generalization, known as Boyle's Law, is usually stated thus:

If the temperature does not change, the volume of a gas varies inversely as the pressure exerted.

585. Use of Boyle's Law in the Correction of Gas Volumes. — Boyle's Law, like Charles' Law, enables us to calculate the volume of a given quantity of gas under new conditions. For example, a quantity of gas has a volume of 120 c.c., the barometer standing at 740 mm. What will be the volume when the atmospheric pressure has increased until the barometer stands at 760 mm.?

The numbers 740 mm. and 760 mm. are measures of the two pressures. The new volume will be found by multiplying the original volume by the ratio of these two numbers. It is apparent that the gas will be subjected to a greater pressure under the new condition. According to the law, its volume will be less. The fraction will therefore have the less number as the numerator. Hence:

$$v = 120 \text{ c.c.} \times \tfrac{740}{760}$$
$$= 116.8 \text{ c.c.}$$

586. Correction for Pressure. — The standard pressure for measuring gases is the pressure that the atmosphere exerts when the barometer stands at 760 mm. This is the average height of the barometer at sea level. The operation of finding the volume of a gas at this pressure is called *correcting the gas for pressure.* The volume of a gas at any pressure whatever is found in a similar manner.

Example: A quantity of air measures 82.2 c.c. at 520 mm. pressure. What will be the volume at 800 mm., the temperature remaining constant?

It is evident that the resulting volume will be less than the original, since the pressure under the new condition is increased. Hence the ratio by which the original volume is multiplied must be less than one.

$$v = 82.2 \text{ c.c.} \times \tfrac{520}{800}$$
$$= 53.4 \text{ c.c.}$$

587. Simultaneous Correction for Temperature and Pressure. — These two corrections can be carried out in one arithmetical operation, for the temperature effect and the pressure effect are entirely independent of each other. For example, a quantity of gas measures 206 c.c. at a temperature of 22° and a pressure of 750 mm. What will be the volume of the gas under standard conditions of temperature and pressure?

$$v = 206 \text{ c.c.} \times \underset{\text{correction}}{\tfrac{273}{295}} \times \underset{\text{correction}}{\tfrac{750}{760}}$$
$$= 188.1 \text{ c.c.}$$

588. Correction for Difference in Level. — Gases are usually measured in bottles or tubes that stand over liquids. The liquid, as a rule, is either water or mercury. In order that the pressure of the gas inclosed under these conditions shall be equal to the atmospheric pressure, the levels of the liquid outside and inside the tube must be the same (Fig. 237). This condition is usually realized by adjusting the apparatus. Sometimes this is impossible, and it is then necessary to correct for the difference in level. This is done by adding to, or subtracting from, the height of the barometer a suitable number. When the inside level is the higher, the pressure on the inclosed gas is less than atmospheric (Fig. 238), for part of the atmospheric pressure is used in supporting the column

of liquid in the tube; when the level of the liquid inside the tube is the lower, the pressure is greater than atmospheric (Fig. 239). For mercury, the actual difference in millimeters is added or subtracted; for water, one thirteenth of this value is used, since water is about one thirteenth as heavy as mercury.

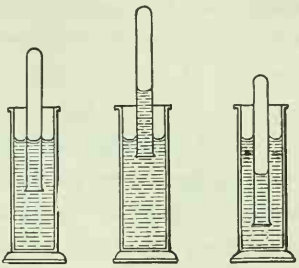


FIG. 237. FIG. 238. FIG. 239.

Different conditions that may exist in measuring gases. In Figures 238 and 239 the pressure is not equal to atmospheric.

Example: A volume of gas is inclosed in a tube over mercury (Fig. 240). The volume of gas measures 68.3 c.c., and the level of the mercury inside the tube is 114 mm. *above* the level in the dish. The thermometer reads 20° C. and the barometer 766 mm. Find the volume of the gas at standard conditions.

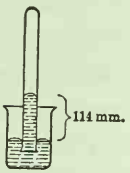


FIGURE 240.

The pressure is less than that of the atmosphere because the downward push of the mercury inside partly balances the pressure of the air.

The corrected pressure is found by *subtracting* 114 mm. from 766 mm.,

$$766 - 114 = 652 \text{ mm.}$$

The gas volume will be corrected to standard conditions as follows:

$$v = 68.3 \text{ c.c.} \times \tfrac{273}{293} \times \tfrac{652}{760}$$
$$= 54.6 \text{ c.c.}$$

589. Correction for Pressure of Water Vapor. — When a gas is confined over water, some of the water evaporates and mixes with the gas. In such a case the pressure of the gaseous mixture consists of two parts, one due to the gas itself

and the other due to the water vapor. The total pressure is the sum of these two pressures. The pressure due to water vapor, therefore, must be subtracted from the observed barometric pressure in order to determine the actual pressure of the dry gas. The pressure due to water vapor depends only on temperature, and not on any other conditions of the experiment. It is always the same for the same temperature, provided the gas is saturated with water vapor. Tables of these values for different temperatures have been prepared as the result of careful experiments. (See page 587.)

Corrections for difference in level and for the pressure of the water vapor (which is sometimes called *aqueous tension*) are both pressure corrections. They are made by adding to or subtracting from the observed barometric pressure suitable numbers. These corrections are parts, then, of the pressure correction.

Example: 24.6 c.c. of nitrogen is contained in a tube over water. The level of the water inside the tube is 27 mm. above the outside level. The barometer stands at 762 mm., and the thermometer at 23°. What is the corrected pressure? On consulting a table we find that the pressure of aqueous vapor at 23° is approximately 21 mm. The corrected pressure is therefore:

$$762 - \underset{\text{Difference in level}}{\tfrac{27}{13}} - \underset{\text{Aqueous tension}}{21} = 739 \text{ mm.}$$

In reducing the fraction for the difference in level, the nearest whole number of millimeters is taken as the result. The error involved is less than that which may occur in reading the volume or the barometer.

590. The following example will illustrate in full the operation of correcting gas volumes:

OBSERVATIONS

Volume of air	79.3 c.c.
Barometic pressure	764 mm.
Temperature	21° C.
Difference in water level (Fig. 238) . .	+41 mm.
Aqueous tension at 21°	18 mm.

The corrected pressure is

$$764 - \underset{\text{Difference in level}}{\frac{41}{13}} - \underset{\text{Aqueous tension}}{18} = 743 \text{ mm.}$$

$$21° \text{ C.} = 294° \text{ abs.}$$

If the temperature of the gas were changed from 294° absolute to 273° absolute, its volume would become less. Hence the ratio for the temperature correction is $\frac{273}{294}$. Changing the pressure from 743 to 760 mm. would also tend to diminish the volume; the pressure correction ratio is, then, $\frac{743}{760}$. The corrected volume is, therefore:

$$v = 79.3 \text{ c.c.} \times \frac{273}{294} \times \frac{743}{760}$$
$$= 71.9 \text{ c.c.}$$

EXERCISES

1. A quantity of hydrogen measures 53 c.c. at a temperature of 20°. What would it measure at 28°?

2. What volume would 60 c.c. of oxygen, measured at 17°, occupy at 0°?

3. Find the volume 65 c.c. of air would occupy, if its temperature were changed from − 13° to 23°.

4. 105 c.c. of oxygen at 27° were cooled to 17°. Find the new volume.

5. What volume would 39 c.c. of air occupy when its pressure changes from 768 mm. to 750 mm.?

6. 38 c.c. of a gas were measured at 744 mm. pressure. Find the volume at 760 mm.

7. 80.2 c.c. of air stand in a tube, mercury levels adjusted; the barometer stands at 768 mm. The next day it reads 755 mm. What volume would the air then have?

8. 151 c.c. of nitrogen gas stand in a tube over water, with the inside level 139 mm. above the outside level. What volume would the gas have if the two levels were the same, the temperature being unchanged? The barometer stands at 754 mm.

9. How much would 52.2 c.c. of air measure if the barometric pressure changed from 750 mm. to 762 mm.? If the temperature also changed from 18° to 25°?

10. A quantity of air and water vapor, standing over water in a gas-measuring tube, levels adjusted, has a volume of 31.8 c.c. The temperature is 26°; the barometer stands at 737.6 mm. Correct the volume of air to standard conditions.

11. A quantity of air and water vapor in a tube over water, levels adjusted, measures 43 c.c. The thermometer stands at 24°, the barometer at 770 mm. Correct to standard conditions.

Correct the following volumes to standard conditions:

	Volume	Conditions	Temperature	Barometer
12.	152 c.c.	Over mercury; levels the same.	27°	755 mm.
13.	1.26 c.c.	Over water; levels the same.	20°	748 mm.
14.	210 c.c.	Over water; inside level 80 mm. above outside level.	22°	764 mm.
15.	15.2 c.c.	Over mercury; inside level 30 mm. above outside level.	21°	760 mm.
16.	129 c.c.	Over water; levels the same.	17°	770 mm.

17. A volume of gas (dry) measures 58.5 c.c. at a temperature of 183° and a barometric pressure of 759 mm. Find the volume of the gas under standard conditions.

18. Why does a tire sometimes burst when a bicycle has been left standing in the sun on a hot day?

PRESSURE OF WATER VAPOR OR AQUEOUS TENSION
(in millimeters of mercury)

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10.0° C.	9.2 mm.	20.0° C.	17.4 mm.
11.	9.8	21.	18.5
12.	10.5	22.	19.7
13.	11.2	23.	20.9
14.	11.9	24.	22.1
15.	12.7	25.	23.5
16.	13.5	26.	25.0
17.	14.4	27.	26.5
18.	15.4	28.	28.1
19.	16.4	29.	29.8
		30.	31.6

APPENDIX

I. PHYSICAL CONSTANTS OF THE IMPORTANT ELEMENTS

Element	Symbol	Atomic Weights		Atomic Number	Valence	Specific Gravity		Melting Point	Boiling Point
		Approximate	Exact O = 16			Water = 1	Air = 1	° C.	° C.
Aluminum	Al	**27**	26.97	13	+ 3	2.7		660	1800
Antimony	Sb	**120**	121.77	51	+ 3, − 5	6.7		630.5	1380
Argon	A	**40**	39.91	18	0		1.38	− 189.2	− 186
Arsenic	As	**75**	74.96	33	+ 3, − 5	5.7		...	615.S
Barium	Ba	**137**	137.37	56	+ 2	3.5		850	1140
Bismuth	Bi	**209**	209.00	83	+ 3	9.8		271	1450
Boron	B	**11**	10.82	5	+ 3	2.0		2300	(2550)
Bromine	Br	**80**	79.92	35	− 1	3.12		− 7.2	59
Cadmium	Cd	**112**	112.41	48	+ 2	8.6		321	767
Calcium	Ca	**40**	40.07	20	+ 2	1.55		810	1170
Carbon	C	**12**	12.00	6	+ 4, − 4	2.26 G		3500	4200
Chlorine	Cl	**35.5**	35.46	17	− 1		2.49	− 101.6	− 34.6
Chromium	Cr	**52**	52.01	24	+ 3, + 6	7.1		1615	2200
Cobalt	Co	**59**	58.94	27	+ 2	8.9		1480	2900
Copper	Cu	**63.6**	63.57	29	+ 1, + 2	8.93		1083	2300
Fluorine	F	**19**	19.00	9	− 1		1.3	− 223	− 187
Gold	Au	**197**	197.20	79	+ 1, + 3	19.3		1063	2600
Helium	He	**4**	4.00	2	0		0.14	< − 272.2	− 268.9
Hydrogen	H	**1**	1.008	1	+ 1		0.07	− 259.1	− 252.7
Iodine	I	**127**	126.93	53	− 1	4.93		113.5	184
Iron	Fe	**56**	55.84	26	+ 2, + 3	7.86		1535	3000
Lead	Pb	**207**	207.20	82	+ 2	11.34		327.5	1620
Lithium	Li	**7**	6.94	3	+ 1	0.53		186	> 1200
Magnesium	Mg	**24**	24.32	12	+ 2	1.74		651	1110
Manganese	Mn	**55**	54.93	25	+ 2	7.2		1260	1900
Mercury	Hg	**200**	200.64	80	+ 1, + 2	13.546		− 38.8	356.9
Neon	Ne	**20**	20.20	10	0	0.696		− 249	− 245.9
Nickel	Ni	**58.7**	58.69	28	+ 2	8.9		1452	2900
Nitrogen	N	**14**	14.01	7	− 3, + 5		0.97	− 209.8	− 195.8
Oxygen	O	**16**	16.00	8	− 2		1.10	− 218.4	− 183
Phosphorus	P	**31**	31.02	15	− 3, + 5	1.8 Y		44.1	280
Platinum	Pt	**195**	195.23	78	+ 4	21.45		1755	4300
Potassium	K	**39**	39.10	19	+ 1	0.86		62.3	760
Radium	Ra	**226**	225.95	88	+ 2	(5)		(960)	(1140)
Radon	Rn	**222**	222.00	86	0		7.5	− 71	− 62
Silicon	Si	**28**	28.06	14	+ 4	2.4		1420	2600
Silver	Ag	**108**	107.88	47	+ 1	10.5		960	1950

S = sublimes; G = graphite; Y = yellow phosphorus; ( ) = estimated.

I. PHYSICAL CONSTANTS OF THE IMPORTANT ELEMENTS — (*Continued*)

Element	Symbol	Atomic Weights		Atomic Number	Valence	Specific Gravity		Melting Point	Boiling Point
		Approximate	Exact O = 16			Water = 1	Air = 1	° C.	° C.
Sodium	Na	**23**	23.00	11	+ 1	0.97		97.5	880
Strontium	Sr	**87**	87.63	38	+ 2	2.6		800	1150
Sulphur	S	**32**	32.06	16	− 2, + 6	2.07		112.8	444.6
Tin	Sn	**119**	118.7	50	+ 2	7.31		231.8	2260
Tungsten	W	**184**	184.00	76	+ 6	19.3		3370	5900
Zinc	Zn	**65**	65.38	30	+ 2	7.14		419	907

II. PHYSICAL CONSTANTS OF COMMON GASES

	Formula	Molecular Weight	Density	Specific Gravity	Solubility in 1 Volume of Water
Acetylene	C_2H_2	26.0	1.17	0.906	—
Air	—	—	1.293	1.00	—
Ammonia	NH_3	17.0	0.771	0.596	727.
Argon	A	39.9	1.78	1.379	—
Carbon dioxide	CO_2	44.0	1.98	1.53	1.00
Carbon monoxide	CO	28.0	1.25	0.967	—
Chlorine	Cl_2	70.92	3.21	2.49	1.5
Helium	He	4.	0.178	0.138	—
Hydrogen	H_2	2.016	0.0898	0.069	0.02
Hydrogen chloride	HCl	36.47	1.64	1.27	464.
Hydrogen sulphide	H_2S	34.08	1.54	1.19	2.5
Methane	CH_4	16.0	0.717	0.554	0.05
Nitric oxide	NO	30.0	1.34	1.037	0.07
Nitrogen	N_2	28.02	1.25	0.97	0.02
Nitrous oxide	N_2O	44.02	1.98	1.53	1.3
Oxygen	O_2	32.00	1.429	1.105	0.05
Sulphur dioxide	SO_2	64.17	2.93	2.26	44.

The values above are experimentally determined.
Density is given for grams per liter.
Specific gravity is the density compared with that of air.
Solubility is the number of volumes of the gas dissolved in 1 volume of water, at ordinary temperatures.

III. TABLE OF SOLUBILITIES

S = soluble in water. I = insoluble in water. P = slightly soluble in water. Ia = insoluble in water and dilute acids

	Aluminum	Ammonium	Antimony	Arsenious	Barium	Bismuth	Cadmium	Calcium	Cobalt	Copper	Ferrous (Fe^{++})	Ferric (Fe^{+++})	Lead	Magnesium	Manganese	Mercurous (Hg^{+})	Mercuric (Hg^{++})	Nickel	Potassium	Sodium	Silver	Zinc
Acetate	S	S	—	—	S	—	S	S	S	S	S	—	S	S	S	P	S	S	S	S	S	S
Bromide	S	S	P	S	S	P	S	S	S	S	S	S	P	S	S	I	S	S	S	S	Ia	S
Carbonate	—	S	—	—	I	I	I	I	I	I	I	—	I	S	I	I	I	I	S	S	I	I
Chlorate	S	S	—	—	S	—	S	S	S	S	S	—	S	S	S	S	S	—	S	S	S	S
Chloride	S	S	P	S	S	P	S	S	S	S	S	S	P	S	S	I	S	S	S	S	Ia	S
Chromate	—	S	—	—	I	I	—	I	I	I	—	—	Ia	S	—	P	P	—	S	S	I	—
Hydroxide	I	S	P	S	S	I	I	P	I	I	I	I	I	I	I	—	I	I	S	S	—	I
Iodide	S	S	P	P	P	I	S	S	S	—	S	—	I	S	S	I	I	S	S	S	Ia	S
Nitrate	S	S	—	—	S	S	S	S	S	S	S	S	S	S	S	I	S	S	S	S	S	S
Oxide	I	—	I	P	S	I	I	P	I	I	I	I	I	I	P	I	I	I	S	S	I	I
Phosphate	I	S	—	—	I	I	I	P	S	S	S	Ia	Ia	S	S	P	S	S	S	S	P	S
Sulphate	S	S	—	—	Ia	S	Ia	P	I	Ia	P	—	Ia	S	I	Ia	Ia	I	S	S	Ia	I
Sulphide	—	S	Ia	Ia	S	Ia	Ia	P	I	S	P	—	I	P	—	—	—	I	S	S	S	P
Sulphite	—	S	—	—	I	—	S	P	I	S	P	—	I	P	—	—	—	I	S	S	S	P

IV. GENERAL RULES FOR SOLUBILITY

Certain generalizations can be made concerning compounds shown in the table on page 592. The exceptions to these generalizations are few and unimportant.

1. All *sodium*, *potassium*, and *ammonium* compounds are *soluble* in water.

2. All *nitrates*, *chlorates*, and *acetates* are *soluble* in water.

3. All *chlorides* are *soluble*, except those of silver, mercury (mercurous), and lead (lead slightly soluble).

4. All *sulphates* are *soluble*, except those of lead, barium, strontium, and calcium (calcium slightly soluble). The silver and the mercurous sulphates are only moderately soluble.

5. All *carbonates* are *insoluble*, except those of sodium, potassium, and ammonium.

6. All *oxides* and *hydroxides* are *insoluble*, except those of ammonium, sodium, potassium, and barium; calcium hydroxide is slightly soluble.

V. VOLATILE COMPOUNDS THAT MAY RESULT FROM DOUBLE DECOMPOSITIONS

1. Compounds volatile at ordinary temperatures:

$$HCl \quad HBr \quad HF \quad H_2S$$

2. Compounds decomposing at ordinary temperatures yielding volatile products:

$$H_2CO_3 \rightleftharpoons (H_2O + CO_2)$$
$$H_2SO_3 \rightleftharpoons (H_2O + SO_2)$$
$$NH_4OH \rightleftharpoons (H_2O + NH_3)$$

3. Compounds volatile below 338° C. (boiling-point of sulphuric acid):

	Boiling Point		Boiling Point
H_2O	100°	HNO_3	86°
HCl (aqueous solution)	110°	HNO_3 (aqueous solution)	120°
HBr (aqueous solution)	126°	$HC_2H_3O_2$	118°

VI. SOLUBILITY OF SOLIDS

Column A gives the number of grams of the anhydrous salt which will dissolve in 100 grams of water at 15° C.

Column B gives the number of grams of the anhydrous salt in 100 grams of water at the boiling point of the saturated solution, given in column C.

	A	B	C
Ammonium chloride . . .	35	87	115°
Barium chloride	35	54	104
Calcium chloride	65	178	150
Calcium hydroxide	.17	.05	—
Copper sulphate	20	60	102
Potassium chloride	33	57	108
Potassium nitrate	26	335	115
Sodium chloride	36	41	109
Sodium sulphate	14	43	103
Sugar	196	—	—

VII. IMPORTANT IONS CONTAINING MORE THAN ONE ELEMENT

Acetate	$(C_2H_3O_2)^-$	Ferrocyanide	$[Fe(CN)_6]^{----}$
Ammonium	$(NH_4)^+$	Ferricyanide	$[Fe(CN)_6]^{---}$
Bicarbonate	$(HCO_3)^-$	Hydroxide	$(OH)^-$
Biborate	$(B_4O_7)^{--}$	Nitrate	$(NO_3)^-$
Bisulphate	$(HSO_4)^-$	Nitrite	$(NO_2)^-$
Borate	$(BO_3)^{---}$	Oxalate	$(C_2O_4)^{--}$
Carbonate	$(CO_3)^{--}$	Phosphate	$(PO_4)^{---}$
Chlorate	$(ClO_3)^-$	Sulphate	$(SO_4)^{--}$
Chromate	$(CrO_4)^{--}$	Sulphite	$(SO_3)^{--}$
Cyanide	$(CN)^-$	Tartrate	$(C_4H_4O_6)^{--}$

VIII. DEGREE OF IONIZATION OF IMPORTANT COMPOUNDS

Showing the fractional part of the solute which is ionized in a solution of the concentration stated, at ordinary temperatures.

Solute	Concentration	Ionization
Nitric acid	normal[1]	0.82
Hydrochloric acid	normal	0.78
Hydrochloric acid	one-tenth normal	0.87
Sulphuric acid	normal	0.51
Oxalic acid	one-tenth normal	0.50
Phosphoric acid	half normal	0.17
Tartaric acid	one-tenth normal	0.08
Acetic acid	one-tenth normal	0.004
Carbonic acid		0.002
Hydrogen sulphide		0.001
Boric acid		0.0001
Potassium hydroxide	normal	0.77
Sodium hydroxide	normal	0.73
Ammonium hydroxide		0.004
Barium hydroxide	normal	0.69
Barium hydroxide	one-tenth normal	0.92
Strontium hydroxide	one-tenth normal	0.93
Calcium hydroxide	one-tenth normal	0.50
Salts[2] of Type $R^{+} A^{-}$	one-tenth	0.85
Salts of Type $R^{+}_{2} A^{--}$	one-tenth	0.72
Salts of Type $R^{++} A^{-}_{2}$	one-tenth	0.72
Salts of Type $R^{++} A^{--}$	one-tenth	0.50

[1] A normal solution contains one gram of replaceable hydrogen (or its equivalent) in one liter of the solution.

[2] R stands for any metal having the valence indicated; A stands for a negative ion with indicated valence.

IX. PRESSURE OF WATER VAPOR, OR AQUEOUS TENSION

(In millimeters of mercury)

Temperature	Pressure	Temperature	Pressure
0.0° C.	4.6 mm.	21.5° C.	19.1 mm.
5	6.5	22.	19.7
10	9.2	22.5	20.3
10.5	9.5	23.	20.9
11	9.8	23.5	21.5
11.5	10.1	24.	22.1
12	10.5	24.5	22.8
12.5	10.8	25.	23.5
13	11.2	25.5	24.2
13.5	11.5	26.	25.0
14	11.9	26.5	25.7
14.5	12.3	27.	26.5
15	12.7	27.5	27.3
15.5	13.1	28.	28.1
16	13.5	28.5	28.9
16.5	14.0	29.	29.8
17	14.4	29.5	30.7
17.5	14.9	30	31.6
18	15.4	40	54.9
18.5	15.9	50	92.1
19	16.4	60	149.2
19.5	16.9	70	233.8
20	17.4	80	355.4
20.5	17.9	90	526.0
21	18.5	100	760.0

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HCl	Hydrochloric	illustration of naming of compounds.
$HClO$	hypochlorous	
$HClO_2$	chlorous	
$HClO_3$	chloric	
$HClO_4$	perchloric	

Commonest O contain compound of an element is given a suffix of ic the first part gives the name of the main element of the acid the acid containing one more O atom than the ic acid is given the prefix per. The acid contains 1 less atom of O than the ic acid is given the suffix ous the acid containing 1 less atom ~~of~~ than the ous acid is given the prefix hypo. the acid contains the hydrogen + the element is given the prefix hydro + the suffix ic.

Table of common IC Acids.

H_2SO_4 sulfuric
HNO_3 Nitric
H_3PO_4 phosphoric
H_3AsO_4 Arsenic
H_3SbO_4 Stibnic (antimonic)
$HClO_3$ chloric
$HBrO_3$ Bromic
HIO_3 iodic

Change of a acid to a salt substitute Na for the hydrogen. the prefix remain the same the suffix change. the ic becoming ate the ous becomes ite.

Strong Acids

HCl HCl
HNO_3 HNO_3
H_2SO_4 H_2SO_4
H_3PO_4 H_3PO_4
HF $HC_2H_3O_2$
H_2CO_3

Strong Bases

NaOH NaOH
KOH KOH
$Ba(OH)_2$
$Ca(OH)_2$
NH_4OH

$Na + HClO_2 \rightarrow NaHClO_2$

Sugar

1. Disaccharides $C_{12}H_{22}O_{11}$

Sucrose (cane & Beet sugars)

Lactose (Milk) Maltose (Malt)

2. Monosaccharides $C_6H_{12}O_6$

Dextrose Levulose

Corn Syrup Honey

A solution is a one-phase system of variable compositions

A phase is a portion of matter separated from other matter by a physical boundary.

Anything you experiment with is a system.

A saturated solution is one in which there is an equilibrium between the solution and the undissolved solute.

7cc $H_2(SO_4)_3$ Gen. Chem
45cc $NaHCO_3$ Smith – Kendall

Mineral

Minerals are those substances of definite chemical composition which are found ready made in the crust of the earth and are not directly products of life or decay of an organism

Contact

$S + O_2 \rightarrow SO_2$

$SO_2 + O \rightarrow SO_3$

$SO_3 + H_2O + H_2SO_4 \rightarrow 2H_2SO_4$

Solvay

$NH_3 + H_2O \rightarrow NH_4OH$

$CO_2 + H_2O \rightarrow H_2CO_3$

$NH_4OH + H_2CO_3 \rightarrow NH_4 + HCO_3 + H_2O$

$NH_4 + HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$NaCl + H_2O + NH_3 + CO_2 \rightarrow NaHCO_3 + NH_4Cl$

Production of CAST IRON

Products Used	Products Formed
Ore	Iron
Coke	Calcium silicate (slag)
Limestone	Gases
Air	

Reactions

$\begin{cases} C + O_2 \rightarrow CO_2 \\ 2C + O_2 \rightarrow 2CO \end{cases}$

$SiO_2 + CaO \rightarrow CaSiO_3$ slag

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

$CaCO_3 \xrightarrow{heat} CO_2 + CaO$

$2(Fe(CO_3)_3 \xrightarrow{heat} Fe_2O_3 + 6CO_2$

Test for:	Add — KSCN	$K_3Fe(CN)_6$	K_4Fe
Ferric ions Fe^{+++}	Red Color	Green	Dar
Ferrous ions Fe^{++}	None	Deep blue	light

In metals the no. of electrons in [illegible]
ring = valene of the atom.
In nonmetals the no of electrons in the outer [illegible]
ring = 8 - the value of the atom
Atoms Combine because they tend to have
an outer ring of 8 electrons

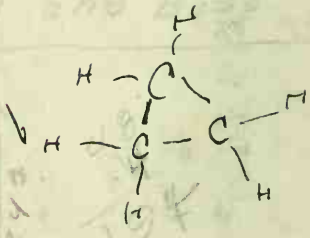
Magnet Metals
Iron + Nickel + Cobalt

Oxidation of an atom is loss
of electrons by that atom

Alcohols
Methane CH_4 — Hydro Carbon
Methyl CH_3OH
Formaldehyde — $HC=O$ — Aldehyde
Ethane C_2H_6 — H. C.
Ethyl C_2H_5OH

N_6
lue
lue

$$\begin{array}{r} .53 \\ 102\overline{)64.00} \\ 510 \\ \hline 300 \end{array} \qquad \begin{array}{r} 200 \\ .53 \\ \hline 600 \\ 1000 \\ \hline 106.00 \end{array}$$



APPROXIMATE ATOMIC WEIGHTS FOR CALCULATIONS

Element	Symbol	Approximate Atomic Weight	Element	Symbol	Approximate Atomic Weight
Aluminum	Al	27	Lead	Pb	207
Antimony	Sb	120	Lithium	Li	7
Arsenic	As	75	Magnesium	Mg	24
Barium	Ba	137	Manganese	Mn	55
Bismuth	Bi	208	Mercury	Hg	200
Boron	B	11	Nickel	Ni	58.7
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Radium	Ra	226
Cobalt	Co	59	Silicon	Si	28
Copper	Cu	63.6	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Strontium	Sr	87
Hydrogen	H	1	Sulphur	S	32
Iodine	I	127	Tin	Sn	119
Iron	Fe	56	Zinc	Zn	65